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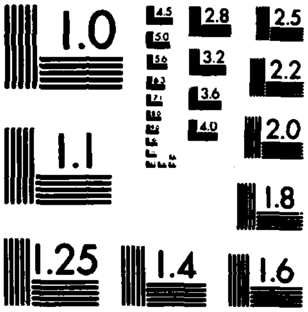

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AFWAL-TR-81-2056
Part II, Vol I

REFINING OF MILITARY JET FUELS FROM SHALE OIL

Part II, Vol I
Preparation of Laboratory-Scale Fuel Samples

H. F. Moore

ASHLAND PETROLEUM COMPANY
ASHLAND RESEARCH AND DEVELOPMENT
ASHLAND, KENTUCKY 41101

MARCH 1982

INTERIM TECHNICAL REPORT FOR PERIOD
JUNE 1979 - OCTOBER 1980

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Shale Oil Refining	Denitrogenation	Guardcase Hydrotreater
JP-4 Jet Fuel	Basic Nitrogen	Aromatic Saturation
JP-8 Jet Fuel	Total Nitrogen	
Hydrotreating	Reforming	
Extraction	Fluid Catalytic Cracking	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Phase II work performed was directed toward the completion of two primary tasks. Task I under this phase was directed at evaluating the effect of operating conditions on material quality, energy balances, product composition, and economics. Task II was directed at obtaining scale-up data for those unit operations of the Phase I process requiring laboratory data to confirm preliminary estimates. Also, nine 500-ml samples of variable quality aviation turbine fuel were produced for evaluation by AFWAL.

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FOREWORD

This project was sponsored by the U. S. Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command, under Contract No. F33615-78-C-2080. The work herein was performed during the period June 15, 1979 to October 30, 1980 under Program Elements 62203F and 63215F, Work Units 30480504 and 24800004, respectively. A discussion of the entire Ashland effort under this contract can be found in a series of six reports entitled "Refining of Military Jet Fuels from Shale Oil", Parts I, II, III, and IV (Part II consists of three volumes). This report is Volume I of Part II which describes the preparation of laboratory-scale fuel samples derived from crude shale oil. The cognizant Air Force Project Scientist was Dr. Ronald D. Butler. We must give recognition to Carolyn Honaker for her assistance in preparing this report.

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ABBREVIATIONS

A	Aromatics
Acid Str	Acid Strength
APL	Aero Propulsion Laboratory
AFWAL	Air Force Wright Aeronautical Laboratories
API	American Petroleum Institute
AQ	Aqueous
AR SAT	Aromatic Saturation Unit
As	Arsenic
ASTM	American Society for Testing and Materials
bbl	Barrel
BN	Basic Nitrogen
$\left(\frac{BN}{TN}\right)_p \left(\frac{BN}{TN}\right)_f$	Ratio of Basic Nitrogen over Total Nitrogen in Product to Basic Nitrogen over Total Nitrogen in Feed
BPD	Barrels per Day
BR NO.	Bromine Number
BS&W	Bottoms, Sediment and Water
BTU	British Thermal Unit
°C	Degrees Celsius
C	Carbon or Heteroatom Concentration
C_1	Methane
C_2	Ethane
C_3	Propane
$C_3^=$	Propylene

ABBREVIATIONS (CONT'D)

$n\text{-}C_4$	Normal Butane
$i\text{-}C_4$	Isobutane
$C_4^{=}$	Butylene
C_5	Pentane
C_5's	Pentane and Pentenes
C_5^{+}	Compounds Heavier than Pentane in Gas Streams
C_6	Hexane
C/H	Carbon to Hydrogen Ratio
cc	Cubic Centimeters
cm	Centimeter
CO	Carbon Monoxide or Cycle Oil
C/O	Catalyst-to-Oil Ratio
COHT	Cycle Oil Hydrotreater
Co/Mo or CoMo	Cobalt Molybdate Catalyst
Cont. Time	Contact Time
Conv.	Conversion
CR	Cracked
CSHT	Crude Shale Hydrotreater
cSt	Centistoke
CW	Cooling Water
E	Activation Energy
EP	End Point in a Distillation
EQ. SUPER DX	Equilibrium Super DX - a cracking catalyst

ABBREVIATIONS (CONT'D)

EXTD	Extracted
°F	Degrees Fahrenheit
FCC	Fluid Catalytic Cracker
FCR	Fluid Catalytic Reactor
Fe	Iron
FI	Flow Indicator
FIA	Fluorescent Indicator Adsorption - Test Method to Determine Hydrocarbon Types
g	Gram
GC	Guardcase Hydrotreater
GC-1	Guardcase Study on In Situ Shale Oil
Gms	Grams
H_2	Hydrogen
HC	Hydrocarbon
HC/N	Ratio of Hydrocarbons to Nitrogen
Hg	Mercury
Hr or hr	Hours
Hr^{-1} or hr^{-1}	Inverse Hours
H_2S	Hydrogen Sulfide
Hydrog.	Hydrogenated

ABBREVIATIONS (CONT'D)

IBP	Initial Boiling Point
I.D.	Inside Diameter
in	Inches
JP-4	Military Specification MIL-T-5624K Turbine Fuel
JP-5	Military Specification MIL-T-5624H Turbine Fuel
JP-7	Military Specification MIL-T-38219 Turbine Fuel
JP-8	Military Specification MIL-T-83133 Turbine Fuel
K_o	Rate Constant
lb	Pound
LCO	Light Cycle Oil
LHSV	Liquid Hourly Space Velocity
LPG	Liquefied Petroleum Gas
LV%	Liquid Volume Percent
MAT	Microactivity Test
MAV	Maleic Anhydride Value
MAX	Maximum
mg	Milligram
MIN or min	Minimum
min	Minute

ABBREVIATIONS (CONT'D)

ml	Milliliter
mm	Millimeter
MT'L	Material
N	Nitrogen
N_o or N_f	Nitrogen in Feed
N_p	Nitrogen in Product
N_a^+	Sodium Ion
Na_2CO_3	Sodium Carbonate
NaOH	Sodium Hydroxide
NH_3	Ammonia
Ni	Nickel
Ni/Mo or NiMo	Nickel Molybdate Catalyst
NO.	Number
NO_x	Oxides of Nitrogen
n-PARAFFIN	Normal Paraffin
O	Olefins
ON SPEC	Meeting Specifications
OXY	Test Series on In Situ Shale Oil
P	Pressure
(P + N)	Paraffins and Naphthenes
PHO	Test Series on Above-Ground Shale Oil

ABBREVIATIONS (CONT'D)

PI	Pressure Indicator
PID Controller	Proportional-Integral-Derivative Controller
ppb	Parts per Billion
ppm	Parts per Million
psia	Pounds of Force per Square Inch Absolute
PSIG or psig	Pounds of Force per Square Inch Gauge
Pt/Al	Platinum/Aluminum Catalyst
Pt/Re	Platinum/Rhenium Catalyst
PV	Parameter Variation
R	Gas Constant
°R	Degrees Rankine
RAFF	Raffinate
RAMS C	Ramsbottom Carbon
RCVY	Recovery
R&D	Research & Development
REF	Reformer
REGEN	Regenerator Section of FCC
RVP	Reid Vapor Pressure
S	Sulfur
SAT	Saturates
SCFB	Standard Cubic Feet per Barrel
SCFH	Standard Cubic Feet per Hour
SIM-D	Simulated Distillation

ABBREVIATIONS (CONT'D)

SR	Straight Run
SS	Stainless Steel
SU or SUS	Saybolt Universal Seconds
TBP	True Boiling Point
TEMP or t	Temperature
TIC	Temperature Indicator and Controller
V	Vanadium
VIS	Viscosity
VOL	Volume
VOl %	Volume Percent
WBS	Work Breakdown Structure
WHSV	Weight Hourly Space Velocity
WT	Weight
WT %, % W, or % WT	Weight Percent

SYMBOLS

=	Equals
+	Positive, plus, or greater than as in 600°F+
-	Negative, minus, or less than as in -600°F
%	Percent
>	Greater Than
<	Less Than
"	Inches
#	Number or Pound
Δ	Difference

SUMMARY

Two whole crude shale oils have been characterized in terms of processability via the EXTRACTACRACKING process. Studies encompassing hydrotreating, fluid catalytic cracking, extraction, and other upgrading steps were accomplished in a manner which provided a broad data matrix for use in computer optimization.

During this program, finished samples of shale-derived turbine fuels targeted to the specifications for JP-4, JP-5, and JP-8 were prepared in addition to a combined JP-4/JP-8 type of fuel. These samples were provided with a range of aromatics content and freeze point, demonstrating the flexibility of this process.

SECTION I

INTRODUCTION

The traditional source of aviation fuels has been the refining of petroleum crude oil. In recent years, the consumption of petroleum products in the United States has exceeded our country's discovery and development of new oil production. The lessening world supply of crude oil, the increased cost of this crude oil, and specifically the dependence of the United States on foreign oil sources were vividly demonstrated during the Arab oil embargo in 1973, as well as the 1979 Iranian crisis. All of these conditions served to emphasize the need for the development of new energy sources within the United States to ensure a continued national energy supply.

A secure and reliable supply of military fuels is essential for our national defense. The Department of Defense and the Department of Energy have set into motion programs for the development of fuels from the coal and oil shale reserves located in the United States. Research and Development efforts have shown that oil derived from shale presents one of the best potential alternate sources of military jet fuels(1). Clearly, the incentive to attain self-sufficiency in aviation turbine fuels is great.

Ashland Research and Development Department of Ashland Petroleum Company has been awarded Contract No. F33615-78-C-2080 to provide sample quantities of aviation turbine fuel, i.e., JP-4 and JP-8, derived from crude shale oil feedstocks for testing and evaluation in programs sponsored by the Aero Propulsion Laboratory (APL) and other participating government laboratories. In order to ascertain the effect of fuel characteristics on equipment components, fuel samples will be produced which will represent possible fuel variations attainable from specified shale oil feedstocks.

Technical work required under this research and development program is concerned with the production of sample quantities of fuels by processes having the potential for scale-up. The processes used to convert whole crude shale oil into military fuels are to be optimized to produce high yields of aviation turbine fuels, type JP-4 or JP-8. It is desired that the process scheme in this research effort be based on the application of promising new refining concepts for increased efficiency and economy.

There are prescribed goals to be pursued under this program. Samples of military fuels shall be provided of various qualities representing fuels which can be economically produced from raw shale oil by methods which shall be disclosed to the Air Force. A complete model of the processing method will be developed to project economic data based on final capacities. This shall represent throughputs which will minimize product costs and maximize overall plant thermal efficiency. One major goal is to present a processing method having a minimum overall efficiency of seventy percent. This energy efficiency shall be based on crude charge, product yield and utility consumptions, including the hydrogen consumption. Finally, a processing method is desired which produces a full slate of military transportation fuels. This slate of fuels shall include motor gasoline, aviation turbine fuels (grade JP-4 or JP-8 and grade JP-5), diesel fuel, diesel fuel marine and residual fuel products. The yields of residual fuel shall be limited to no more than ten percent of the product slate while maximizing the yield of aviation turbine fuel, grade JP-4 or JP-8.

This program is divided into four phases. The objective of the completed initial phase, or Phase I, was directed at the preparation of an overall processing method for the efficient and economic upgrading of whole crude shale oil. The recently completed second phase required that up to five 500-ml samples of various aviation turbine fuels be produced for evaluation at AFWAL. This phase included two tasks. Task I was directed at evaluating the effect of operating conditions on material quality and energy balances and on product compositions and economics. Task II was directed at producing 500-ml samples by these unit operations. Phase III, which is underway at present, is aimed at: (1) confirming final process design estimates proposed in Phase I and (2) producing sample lots of turbine fuel for aircraft component performance evaluations. Finally, Phase IV is an overall optimization study involving computer modeling of shale oil upgrading.

Production of military aviation turbine fuels from whole crude shale oil represents an exciting, challenging research area for the technical community. Although a multitude of problems may be encountered, Ashland feels that these problems can be solved and the goal of aviation fuel production achieved. A proprietary processing plan to achieve this goal has been developed by Ashland Petroleum Research through in-house research on synthetic fuels. The EXTRACTACRACKING process is a combination of refining steps which were specifically designed to economically refine shale oils into JP-4 and JP-8 type fuels.

The approach taken by this process on whole crude shale oil was to refine crude shale oil by a combination of hydrotreating, extraction and fluid catalytic cracking (FCC) steps into streams demonstrating the desired physical and chemical characteristics required for finished fuels. Final product treatment steps, such as reforming and hydrotreating, were provided for the production of specification fuels.

SUMMARY OF PHASE I RESULTS

Phase I of this program commenced on February 15, 1979 and was completed on June 15, 1979. The primary objective of the Phase I program was to perform a preliminary process analysis. The work was directed at the description of an overall processing method based on the application of new and promising concepts for the efficient and economic upgrading of whole crude shale oil. This preliminary process was aimed at demonstrating technical, as well as economic, process feasibility. Under this phase, two overall processing methods were explored: one method producing JP-4 type aviation turbine fuel, the other method producing JP-8 type aviation turbine fuel. Work accomplished under this phase included:

- Schematics of the qualitative process flow diagrams indicating the flow of materials, the unit process operations involved, the apparatus necessary and special information on such operating conditions as temperature, pressure, and liquid hourly space velocity (LHSV).
- Schematics of the quantitative flow diagrams showing the quantities of material for each processor unit operation.
- Schematic drawings of equipment indicating the specified size or capacity of each piece of process equipment and its material(s) of construction.

- Preliminary estimates of the economics, product qualities and product yields.
- Determine the quantity of shale oil required to complete the full program. As a result of this study, we were supplied 14 drums of Paraho crude shale oil and 96 drums of in situ shale oil.
- Prepare preliminary process optimization and computer models.

The results of this study(2) show that the EXTRACTA-CRACKING process efficiently addresses the problems encountered in processing shale oil to jet fuel. The process follows a scheme which maximizes jet fuel production and allows flexibility in meeting final product specifications and yield structure.

Objectives of the process were fully met in this analysis. The quantity of jet fuel (JP-8) was maximized at 62.3% (vol.) of the product slate. This corresponds to 54.4% (vol.) of the shale oil charged. Gasoline, another prime product, was 32.0% (vol.) of the product slate, which is 28.0% (vol.) of the shale oil feed. Burner fuel was minimized at 5.7% (vol.) of product slate and 5.0% (vol.) of shale oil feed. Recovery of prime products based on shale oil feed was 87.4% (vol.). The prime product slate is outlined in Table I-1, with an overall recovery of 95% (vol.) of shale oil charge when all products are included.

Inspections of prime products indicate military fuel specifications should be met or exceeded. Gasoline, JP-8

TABLE I-1

OVERALL MILITARY FUEL YIELDS

JP-8 EXTRACTACRACKING

	BPD	VOLUME % OF PRIME PRODUCTS	VOLUME % OF FEED
GASOLINE	27,986	32.0	28.0
JP-8	54,444	62.3	54.4
BURNER FUEL	4,997	5.7	5.0
TOTAL	87,427	100.0	87.4

BASIS: 100,000 BPD CRUDE IN SITU SHALE OIL CHARGE or JP-4 turbine fuel, and burner fuel military specifications were calculated to be met or exceeded in all cases.

Since the EXTRACTACRACKING process contains a great degree of flexibility, properties can be easily adjusted according to the desired specification range. As an example, if turbine fuel aromatic content specifications are altered in the future, the process can be adjusted to produce the desired product at a lower cost. Freeze point also can be adjusted to meet the desired specification.

These results, along with the tailored distillation range, showcase the ability of the EXTRACTACRACKING process to produce both JP-8 and JP-4 and to meet any future military specification fuels which would be desired.

Finally, economic results from the Phase I study indicate that the cost of producing prime military fuels would be at least competitive with published results(3), and demonstrate a strong potential for increased cost effectiveness. Cost distribution for products from EXTRACTACRACKING, as estimated during Phase I, is shown in Table I-2. As is common for synthetic fuels plants, the primary input cost factors are feedstock and capital. These items made up over ninety percent of the total finished product cost.

Results from this Phase I study were utilized to define uncertainties in the calculation and isolate particular areas for attention during Phase II. Section II describes the overall EXTRACTACRACKING concept, and the following sections describe the Phase II experimental efforts.

TABLE I-2

PRODUCT COST DISTRIBUTION

JP-8 EXTRACTACRACKING

PHASE I

ITEM	PERCENT OF TOTAL COST
STARTUP	0.2
WORKING CAPITAL	1.6
UTILITIES	4.4
LABOR AND OVERHEAD	4.5
BY-PRODUCTS	(5.1)
CAPITAL	21.6
FEEDSTOCK	72.8

SECTION II

PROCESS DESCRIPTION

BACKGROUND

The EXTRACTACRACKING process is the outgrowth of many years of proprietary research into refining of petroleum as well as synthetic liquids. Classically, any process used for conversion of synthetic materials into a conventional fuel product slate has suffered from two major drawbacks: (1) the refining technology used was essentially conventional petroleum refining operations requiring initial conversion of the synthetic material into a petroleum-like stream and (2) conventional product slates and properties have evolved over many years, in great part due to the characteristics of petroleum rather than any inherent advantage to the specific result attained. The EXTRACTACRACKING process was designed in particular to address these problems, and, while item (2) is a constraint not easily modified, maximization of the use of natural boiling-range products is used in that area to improve the process efficiency.

Shale oil refining has received a tremendous amount of attention in previous years. In fact, the primary constraint to the use of oil shale resources will probably be production and transportation of the crude shale oil rather than any required refining modifications. Refining technology is available, although the required equipment may not be, for producing finished fuel products from raw shale oil.

The status of present shale oil refining technology may be classified into three key processing areas: delayed coking, hydrocracking, and fluid cracking. The key processing area for each of these methods has invariably been high severity hydrotreating, either prior to or after the conversion step. Each of these methods has negative features, particularly in an economic sense. Delayed coking produces a relatively high yield of low or zero value coke product. Hydrocracking provides high yields of products, but at high capital and operating cost. Fluid cracking may suffer from catalyst poisoning by high levels of basic nitrogen compounds, although published work is relatively sparse in this area. In each of these areas, the high cost of the (assumed) requirement of concurrent high severity hydrotreating is a negative factor.

Each of these areas was examined in detail during development of the EXTRACTACRACKING process. In some cases, it has been necessary, or at least desirable, to discard conventional petroleum processing philosophies in order to more accurately develop an improved shale oil refining process.

PROCESS OBJECTIVES

Review of the technical literature, and a significant quantity of proprietary research, has led to the conclusion that new, novel processing is both necessary and desirable for improved refining of shale oil. Again, the point must be emphasized that, given proper equipment capabilities and an adequate source of capital, the generic processing schemes described above are, in all probability, viable technical methods of converting crude shale oil to finished fuels. However, processing shale oil under petroleum processing constraints places a severe penalty on this material as a fuels feedstock.

With these factors in mind, the following objectives for developing a new shale oil refining process were delineated:

> "Provide an overall processing method for conversion of whole crude shale oil into finished, conventional fuels. The process should be capable of efficient operation on a wide range of shale feedstocks, in particular both in situ and above-ground retorted materials. Specific problems inherent to shale oil must be directly addressed, and the overall philosophy should be to take advantage of shale oil's differing character from petroleum, rather than accepting a penalty for that difference."

In all cases, implicit constraints within these objectives are that the process be technically viable, as well as economically competitive with other alternative methods.

PROCESS DESIGN CRITERIA

As the first step towards meeting these objectives, the key properties of several crude shale oils were defined. Table II-1 demonstrates an open literature comparison of these properties(4). Further, since we have at least implied that conventional refineries are generally unacceptable for refining of crude shale oils, these data were compared to petroleum stocks such as those shown in Table II-2(5). Comparison of these data, and generalization of specific source characteristics, led directly to a relatively concise statement of the problems involved as shown in Table II-3 and discussed below.

When compared with conventional petroleum stocks, shale oil is high in heteroatom (sulfur, nitrogen and oxygen) content. Sulfur may or may not be considered a major problem, as the levels demonstrated may be equivalent to or lower than specific petroleum materials. As a minimum, however, the sulfur contents are of a magnitude which require removal prior to use of the finished fuels. Extremely high oxygen contents are routinely exhibited by shale oils. While oxygen also may or may not present a major problem to shale oil refiners, specific design requirements addressing its concurrent removal and/or handling must be factored into any successful processing method. Finally, and of most concern, shale oils exhibit very high nitrogen content. When

TABLE II-1

PROPERTIES OF SHALE OILS FROM DIFFERENT RETORTING PROCESSES(1)

	Paraho	Tosco	Garrett
Gravity, °API	19.3	21.0	25.0
Sulfur, Wt. %	0.71	0.67	0.64
Mercaptan Sulfur, ppm_w	56	47	39
Nitrogen, Wt. %	2.00	1.85	1.30
Pour Point, °F	85	70	50
Salt Content, PTB	0.9	-	1.0
Viscosity, cSt			
@ 100°F	78.5	27.1	15.8
@ 122°F	42.6	-	9.93
Fraction Yields, Volume Percent			
IBP-302°F	0	6.3	1.0
302-401°F	1.5	8.1	3.7
401-650°F	23.4	20.6	41.1
650-1050°F	66.1	47.4	49.7
>1050°F	9.0	17.6	4.5

TABLE II-2

TYPICAL CRUDE PETROLEUM STOCKS

Properties	Alaskan North Slope (Prudhoe Bay Common)	Mid Continent (Louisiana-Mississippi Sweet)	Mid East (Arabian Light)	North Sea (Ekofisk)
Full Range Crude				
Gravity, °API	26.8	38.5	34.0	38.5
Characterization Factor	11.69	12.13	11.98	12.06
Pour Point, °F	+30	+30	-5	0
Sulfur Content, Wt. %	1.00	0.15	1.65	0.18
170-400°F Fraction				
Vol. % Crude Basis	16.2	26.5	22.1	25.6
Gravity, °API	49.4	34.9	55.6	53.5
Basic Nitrogen, Wt. %	0.001	<0.0001	<0.0001	<0.0001
Sulfur, Wt. %	168 (ppm)	46 (ppm)	314 (ppm)	38 (ppm)
Vol. % Paraffin	43.62	57.85	72.59	55.66
Vol. % Olefin	0.13	0.07	0.22	0.05
Vol. % Naphthene	38.48	37.60	14.08	30.94
Vol. % Aromatic	17.77	4.48	13.11	13.35
Acid Number	0.08	0.06	0.14	<0.01
375-480°F Fraction				
Vol. % Crude Basis	9.8	12.7	11.2	11.5
Gravity, °API	38.5	43.8	45.1	42.8
Basic Nitrogen, Wt. %	0.001	0.0001	0.0003	0.0002
Sulfur, Wt. %	0.10	176 (ppm)	0.20	172 (ppm)
Smoke Point, mm	17.0	25.0	22.0	24.0
Aniline Point, °F	133.0	159.5	150.0	148.5
Acid Number	0.07	0.03	0.01	0.02

TABLE II-3

MAJOR PROBLEMS IN SHALE OIL PROCESSING

- NITROGEN
- OXYGEN
- SULFUR
- ARSENIC
- NORMAL PARAFFINS
- CONJUGATED DIOLEFINS
- METALS
- TRAMP METALS AND FINES FROM RETORTING
- BOILING RANGE DISTRIBUTION

evaluated in terms of conventional refining, nitrogen is a severe poison for many refinery catalysts. In terms of a finished fuel, nitrogen levels are also required to be low to minimize NO_x emissions during combustion.

Other elements, in particular the metallic inclusions, are important in shale oil refining. Arsenic is of concern, specifically due to potential health hazards, as well as its known poisoning effect on many refining catalysts. Iron, nickel and vanadium are also present in shale oil to an extent that specific attention must be addressed to their removal prior to processing over catalysts sensitive to those metals.

Since shale oil is produced from a solid material, oil shale fines are commonly encountered. These fines possess the potential for pluggage of fixed catalyst beds, equipment damage and/or catalyst deactivation. Further, the specific production method used may increase expected metals content due to tramp iron inclusion, exacerbating the problems described above.

The relative quantities of hydrocarbon types present in shale oil differs markedly from those routinely encountered in crude petroleum streams. The normal paraffin content of the saturate fraction is uniquely high in shale oil, presenting not only potentially high freeze or pour points in the finished products, but also requiring special design and handling procedures to prevent wax crystallization and/or gellation of the processing streams. Olefin and diolefin content of shale materials is also high, resulting in high hydrogen consumption in any hydrotreating step, as well as leading to a marked tendency towards coke formation during initial heating steps.

Finally, the boiling range distribution of shale oils is quite different from those encountered with petroleum. Generally, shale oils are characterized by high percentage yields of heavy gas oil materials, specifically those fractions heavier than the high value, high demand light distillate products normally required. Alternatively stated, the straight run yields of light distillate products are inadequate to meet present market demand and require boiling range conversion to a greater degree than most petroleum stocks.

These generalized characteristics of shale oils were used as the foundation for specific process design of a conceptually improved process. They are based primarily on technical grounds and, as such, are of key importance to any process. However, any successful process must satisfy not only technical requirements, but also meet relative economic constraints as well. Evaluation of the present generation of shale oil refining processes indicates that, in general, the major economic factors may be characterized as capital and operating costs.

Capital costs are important because of the necessity for investment prior to production and the associated capital recovery and equitable rate of return requirements over the productive life of the asset. Previous processes have demonstrated high capital costs due in large part to the extremely high severities utilized, and in particular, the use of large, high-pressure equipment. Reduction in both vessel size and operating pressure requirements could reduce capital costs significantly.

The primary operating cost factor in shale oil processing has classically been hydrogen consumption. The necessity or result of adding 2000 to 3000 standard cubic feet of hydrogen per barrel of crude shale oil has become a routine datum in processing studies. Reduction of this requirement should result in lower capital costs due to smaller hydrogen generation facility requirements, as well as lower operating severity, reduced capital costs as noted above, in addition to reduced operating difficulties and associated process downtime.

Consideration of these economic factors leads to a further general philosophy in development of an improved process: wherever possible, low-severity, relatively low pressure processes should be used. Hydroprocessing should be minimized, used only where alternative methods are not viable, and for those cases where necessary should be operated at minimum process severity.

Further factors, such as plant operability, offsites and location are important in specific cases. The factors discussed above, however, are items generally considered to be of key importance in shale oil refining, and have been used in development of the EXTRACTACRACKING process.

THE EXTRACTACRACKING PROCESS

EXTRACTACRACKING is an integrated process specifically designed for conversion of non-conventional feedstocks into only finished, conventional products. In the configuration addressed in this program, EXTRACTACRACKING directly addresses the problems involved in shale oil refining described previously.

The process configuration evaluated in this program is shown schematically in Figure II-1. Whole crude shale oil is converted by a combination of hydrotreating, extraction and fluid cracking steps into a crude distillate stream demonstrating the desired boiling range characteristics, as well as the approximate physical and chemical characteristics required for finished fuel production. Final product treating steps are provided as conceptually necessary for production of finished, on-specification fuels. Since the overall objective of this program is production of an economic maximum of aviation turbine fuels, the processing configuration and conditions delineated herein have been defined for that result. Table II-4 demonstrates the direct correlation between problems anticipated for shale oil refining and the provision of specific processing modules in this design. To define each of these modules further, a step-by-step process description follows.

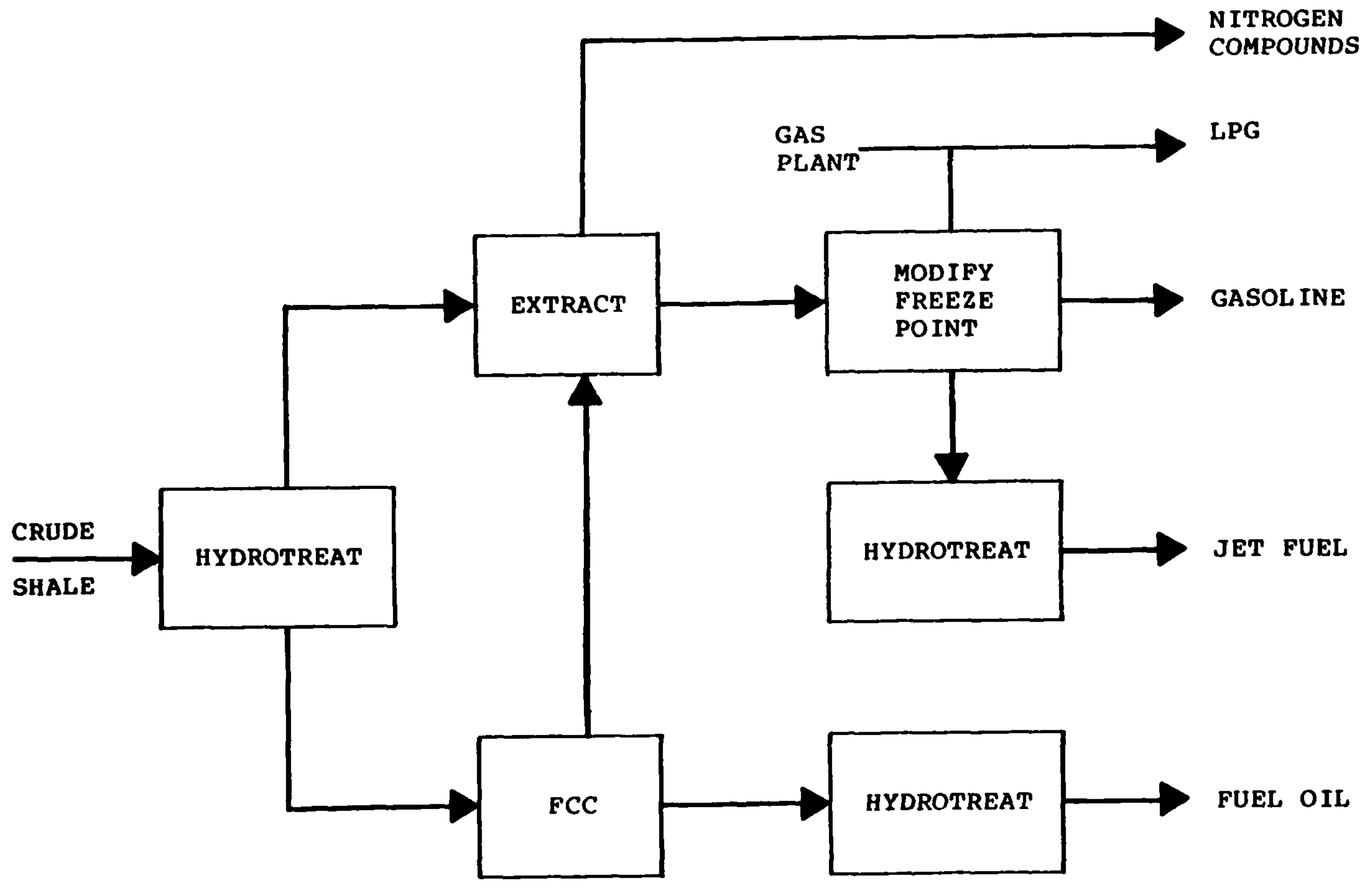

Figure II-1. The EXTRACTACRACKING Process

TABLE II-4

EXTRACTACRACKING'S ANSWER TO SHALE OIL REFINING PROBLEMS

● CRUDE SHALE HYDROTREATING	● SULFUR, ARSENIC, OLEFINS
● FLUID CATALYTIC CRACKING	● BOILING RANGE DISTRIBUTION
● LIQUID EXTRACTION	● NITROGEN, OXYGEN
● GUARDCASE HYDROTREATING	● RESIDUAL AMOUNTS OF SULFUR, NITROGEN, OXYGEN AND ARSENIC
● FREEZE POINT MODIFICATION	● NORMAL PARAFFINS
● FINAL PRODUCT TREATING	● CONVERSION OF ANY ITEM REMAINING DELETERIOUS TO PRODUCT QUALITY

SECTION 100 - CRUDE SHALE HYDROTREATER

Whole crude shale oil is provided from product tankage to the crude shale hydrotreater without pretreatment. In order to ensure a low water, low salt content material, the crude shale is heated and processed through caustic desalting similar to conventional technology. The desalted oil is mixed with recycle plus make-up hydrogen, heated in a feed/effluent heat exchanger and fired heater, and fed upflow to parallel guard bed reactors for arsenic removal. The dearsenated oil is heated to reaction conditions and fed downflow to the hydrotreating reactor.

The hydrotreater effluent is passed through heat recovery and cooling exchangers and to a water-washed high pressure flash drum. Gas from the high pressure flash drum is treated in an aqueous ethanolamine scrubber prior to recycle. The treated gas is then compressed and mixed with make-up hydrogen for recycle. The water phase from the high pressure flash drum, containing significant quantities of ammonia and hydrogen sulfide, is meanwhile sent to the gas plant for treating.

The hydrocarbon phase from the high pressure flash drum is processed through a low pressure flash drum, preflash tower and atmospheric fractionator in a conventional manner. The fuel gas produced is routed to the gas plant for recovery and distillate and gas oil streams provided for further processing.

The major elements of the crude shale hydrotreater are the production of two low-sulfur, low-metal, low-olefin streams at a relatively low level of denitrogenation and hydrogen consumption.

SECTION 200 - FLUID CATALYTIC CRACKING

The gas oil produced in Section 100 is routed to the fluid catalytic cracking (FCC) unit. The specific boiling range provided to the FCC is dependent on the final product streams desired. Due to the low preheat requirements of this unit, and relatively high coke value encountered, feed preheat may be accomplished entirely by feed/effluent exchange. Recycle from Section 400 (cycle oil hydrotreater) is also provided for minimization of residual fuel yields.

Feed is injected at the base of the FCC riser in intimate contact with hot regenerated catalyst. Spent catalyst and oil vapors are disengaged by means of high temperature cyclones.

The spent catalyst first passes through a stripper/standpipe, where residual hydrocarbon is recovered by steam stripping, and then into the regenerator. Due to a relatively high coke yield utilization of high regenerator temperatures, high carbon monoxide (CO) production (limited oxygen), and internal steam coils are required to maintain heat balance. The flue gas is admixed with an adequate quantity of fuel gas to sustain combustion and burned in a CO boiler for control of CO emissions and production of high quality steam.

The FCC unit provides the desired degree of boiling range conversion necessary for maximum economic production of gasoline and turbine fuel fractions. Of primary importance, the unit accomplishes this conversion at low pressure (~25-30 psig) with no external hydrogen source. Further, FCC units in general have been shown to be effective means of desulfurization and denitrogenation, or at least provide selective redistribution of the original heteroatom contents. This module, including, in particular the capability of processing high nitrogen feedstocks, is one major key to success of the process.

Oil vapors from the reactor cyclones are processed through heat recovery, preflash tower and atmospheric distillation. Precise fractionation is not provided. The total gas stream is sent to the gas plant and again, distillate and gas oil (cycle oil) streams are produced.

SECTION 300 - EXTRACTION

The basic EXTRACTACRACKING technology package contains processing modules capable of both nitrogen and oxygen compound extraction. However, after evaluation of pertinent data available on crude and converted shale oil streams, it has been determined that the oxygen extraction sequence is undesirable under present design conditions.

In the extraction section, chemical treatment of the combined distillate streams from the crude shale hydrotreater and FCC units is accomplished in such a manner that a treated naphtha plus distillate, a nitrogen extract, and a marketable by-product are produced. Countercurrent contacting, plus proper operation of previous plant sections, allows up to 80 to 90 percent denitrogenation to be accomplished based on feed/raffinate nitrogen levels.

The extraction section, and its interdependent relationship to prior operations, is the second major key to the EXTRACTACRACKING process. No hydrogen is used in this section, nor is high pressure equipment required. Further, by proper adjustment of the conditions in Sections 100, 200 and 300, high percentage nitrogen removal can be accomplished without hydrogen consumption, while concurrently producing a relatively small by-product extract stream.

These three sections comprise the major conversion and clean-up steps of the process. Major products at this point are a low-nitrogen, low-sulfur gasoline plus turbine or diesel fuel stream, and a moderate-nitrogen, low-sulfur fuel oil stream. If required, operating conditions may be modified to produce essentially no heavy fuel.

In some circumstances, the products from these three sections could be provided to an existing refinery for concurrent petroleum/shale oil processing. The alternative, described below, is to further process these products in the unique EXTRACTACRACKING product treating sections.

SECTION 400 - CYCLE OIL HYDROTREATER

Bottoms from the FCC unit are processed through the cycle oil hydrotreater to produce a low nitrogen, low sulfur fuel oil in addition to providing an upgraded recycle oil stream if desired. The unit is comparable to a conventional gas oil hydrotreater and needs no further description here.

SECTION 500 - GUARDCASE HYDROTREATER

EXTRACTACRACKING provides almost "rheostat" capability for final gasoline and jet fuel product tuning. The capability for providing this tuning is based on relatively sensitive, selective catalysts which must be protected from heteroatom or metals carryover. As a result, a guardcase hydrotreater has been included to provide this protection.

In this program, the guardcase receives a combined extraction raffinate with an endpoint corresponding to the heaviest fuel required to be treated. Essentially quantitative removal of sulfur and nitrogen are provided to less than 1 ppm product specification. Additionally, the unit truly acts as a guard chamber in that any metals carryover, particularly arsenic, will be isolated from the further treating steps.

This unit is a relatively low severity (for synthetic fuels processing) operation, corresponding to conventional gas oil hydrotreating operations or possibly slightly less severity. Feed provisions and product separation are conventional. Gas and reformer charge streams are produced in addition to a foul water stream composed primarily of water from deoxygenation plus wash water injected to the high pressure flash drum. Hydrogen consumption is moderate and corresponds roughly to the net hydrogen produced in Section 600 or less.

SECTION 600 - FREEZE POINT MODIFICATION

A unique EXTRACTACRACKING feature is the ability to selectively modify the anticipated high freeze point of shale-derived turbine fuels. As noted previously, the saturate fraction of crude shale oil routinely is composed of a high level of normal paraffins which have been shown to exhibit high freeze point values. To the extent necessary, these paraffins are either isomerized or dehydrocyclized in a novel, low severity adaptation of conventional reforming operations.

A further advantage to the reforming section at this point is moderate improvement of the gasoline fraction octane value. The combined reformate effluent stream is fractionated into gas, gasoline and heavy reformate streams. The gasoline, which demonstrates a moderate octane number, is sent directly to gasoline blending, while the heavy reformate is further processed in Section 700.

SECTION 700 - AROMATIC SATURATION

The heavy reformate from Section 600 is hydrogenated in a very selective manner to any specified aromatic content. The process has been demonstrated on a commercial basis. Relatively low pressures are utilized while specific hydrogen consumption is moderate, depending on final product requirements, as well as specific operation of preceeding units. It is a selective operation, using only that hydrogen directly required for final product input. Further, compared to the initial crude shale oil stream, the net relative consumption is low.

These seven major sections comprise the body of an integrated EXTRACTACRACKING plant. Separate from the primary plant itself, however, are offsites required to convert the battery limits plant described above into a grass roots efforts. While these offsites are in no way unique to EXTRACTACRACKING, they are necessary for overall operation of the plant. Successful operation of the plant does not require the specific details presented below, as long as the services described are provided.

SECTION 800 - GAS PLANT

The gas plant provided in this program is composed of several major items, including:

- Saturated Gas Plant
- Unsaturated Gas Plant
- Foul Water Treating

- Fuel Gas Treating
- Ammonia Liquefaction

The saturated gas plant receives gases from all plant sections except 200 and 300, and produces a fuel gas (H_2-C_2), LPG, mixed butanes and light gasoline (C_5+) streams. The unsaturated gas plant receives gas from Section 200 and produces fuel gas, a propane/propylene stream, a mixed butane stream and a light gasoline stream. The foul water treating plant receives foul water from all plant sections, recovering process water, ammonia (NH_3) and hydrogen sulfide (H_2S). The fuel gas treating plant scrubs hydrogen sulfide and ammonia from the plant fuel gas and produces a clean fuel gas stream and a mixed H_2S/NH_3 stream, which is routed to Section 900. Finally, the ammonia liquefaction section provides the capability to produce anhydrous ammonia in a form most readily handled and/or sold.

SECTION 900 - SULFUR RECOVERY

The sulfur recovery section receives a high quality H_2S stream from fuel gas treating and a mixed H_2S/NH_3 stream from foul water treating. The unit includes both Claus and tail-gas clean-up, and is available commercially in many forms.

SECTION 1000 - HYDROGEN PLANT

Net hydrogen consumed in the EXTRACTACRACKING process is produced, in this design, by steam reforming of net fuel gas from the gas plant. Fuel gas is also used for plant fired heaters, resulting in a balanced overall fuel gas system. The hydrogen plant is a common commercial unit providing 95 percent purity hydrogen.

A second process option is to provide all or a portion of the plant hydrogen requirements by partial oxidation of the nitrogen extract. Promising, higher value outlets for this stream have been previously defined, but, due to the limited scope of this study, evaluation of these outlets has been severely restricted. At present, the assumption must be made that partial oxidation of this stream will be practiced.

SECTION 1100 - TANKAGE

A significant quantity of tankage is required for any plant of this magnitude. Actual provisions must be made based on specific site and project requirements.

SECTION III

DESCRIPTION OF WORK

The original statement of work, contained in the original contract documents(5), was *followed throughout the* Phase II efforts. An overall schematic of the work breakdown structure is shown in Figure III-1. Tasks I and II, defined in Table III-1, were laboratory studies to develop adequate data for evaluation with preliminary computer work provided for each Task in order to better direct the experimental efforts on an early feedback basis.

Drum quantity samples of shale oil were provided by the Air Force: 14 drums of above-ground retorted oil and 96 drums of in situ retorted oil. These drums were stored in a nearby secure location, under roof, until needed at the experimental facilities. Since the in situ oil was provided in quantities adequate for further processing in Phase III, and since Phases II and III were designed to overlap, expedited processing was provided for the in situ material.

TASK I

Task I was composed of oil characterization, definition of catalytic processing response and definition of chemical processing response. The majority of work required and effort expended was in the area of catalytic processing response.

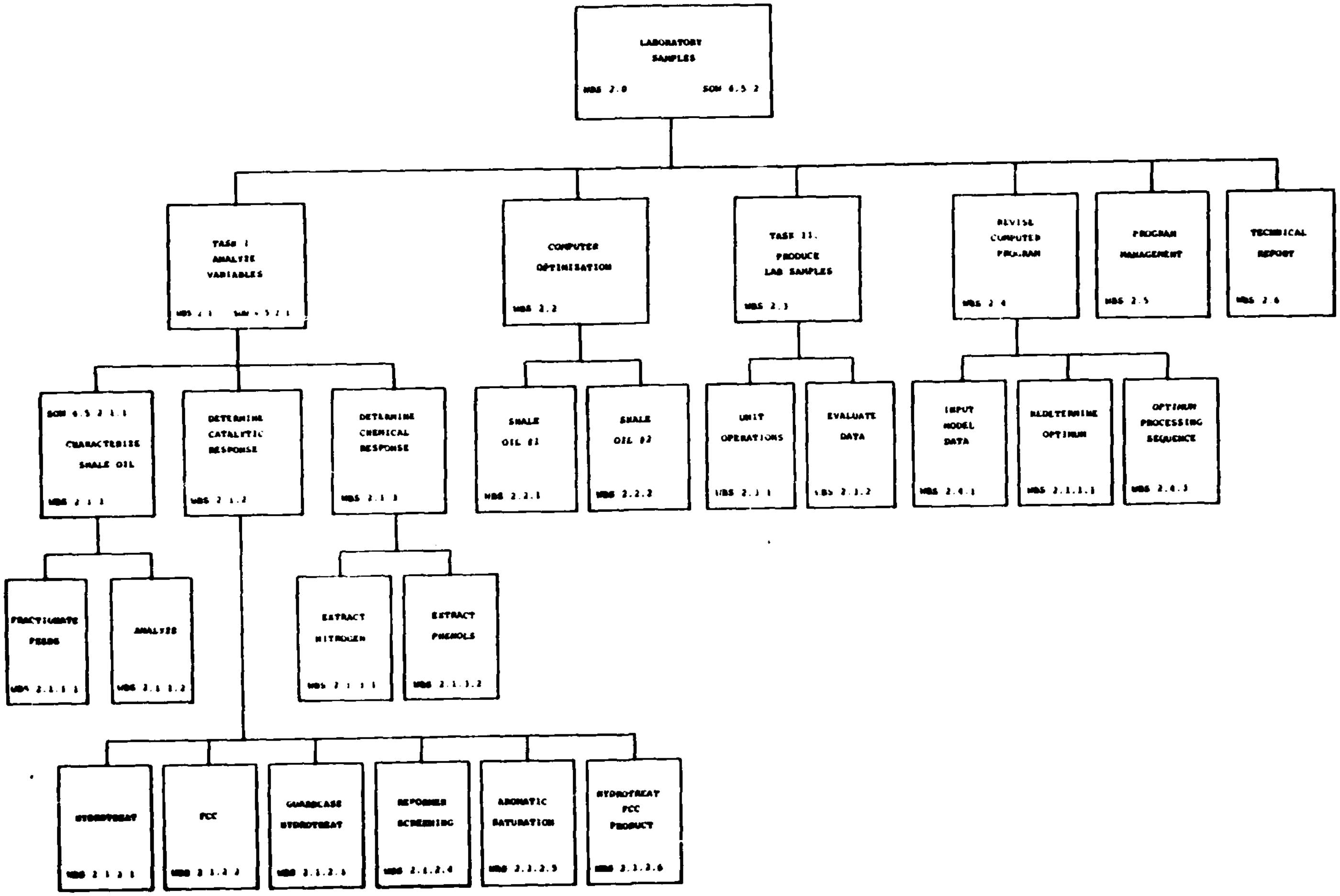

Figure III-1. The Original Phase II WBS Hierarchy Diagram

TABLE III-1

Military Jet Fuel From Shale Oil
Phase II
Task Definition

Task I. Evaluate Process Variables

Task II. Produce 500 Milliliter Fuel Samples

Characterization of each oil was provided by selection of an individual drum, mixing well, and withdrawing a five-gallon sample. This sample was then fractionated into pseudocomponents to 600°F (atmospheric equivalent) on a one-inch Podbielniak packed column. The 600°F+ product was further fractionated into crude pseudocomponents under high vacuum on a Hempel apparatus. Each pseudocomponent was then analyzed for pertinent properties.

Definition of catalytic process response, as noted above, comprised the majority of the Task I effort. Processing studies were provided for the crude shale hydrotreater, FCC, cycle oil hydrotreater, guardcase, reformer and aromatic saturation.

The crude shale hydrotreater received a large amount of attention, both since this unit in most conventional processes defines hydrogen consumption and cost, as well as since all samples for further processing are defined by this step. Initial parameter variation studies of short duration were provided to screen temperature, pressure, space velocity and catalyst response factors. Results from these studies were followed by longer (nominal 5 days) duration tests for confirmation of this data on a lined-out basis. Finally, indicated process severity requirements were evaluated on longer duration (nominal 30 days) catalyst stability evaluations. This full data set provides a maximum quantity of data in a rapid, cost effective manner while providing stabilized, longer term data for verification of short term results. Parameters evaluated are shown in Table III-2.

FCC studies were provided on both micro-scale MAT (microactivity test) units and continuous circulating (FCR) equipment. A large number of pertinent samples from the parameter variation and five-day hydrotreating tests were processed on the MAT unit to provide a wide range of response data, while samples from 5-day and 30-day hydrotreating tests were processed on the FCR. Temperature, catalyst-to-oil ratio, weight hourly space velocity, and feedstock initial boiling point (IBP) were evaluated on these units, as shown in Table III-3, in addition to the feedstock variability factor defined by the differing source hydrotreating efforts. Recycle streams, in addition to fresh feeds, were evaluated.

The guardcase hydrotreater was operated on seven extraction raffinate samples. In each case, a minor amount of parameter variation was practiced in order to define minimum required process severity. A short (12 day) catalyst aging study was also provided for raffinate from each oil. Samples of guardcase product were fractionated into pertinent turbine fuel boiling ranges, and the resulting crude fuel evaluated. Comparison of these properties with turbine fuel specifications was then made to define further

TABLE III-2

MAJOR PARAMETERS EXAMINED FOR THE CRUDE SHALE HYDROTREATER

TEMPERATURE

PRESSURE

LIQUID HOURLY SPACE VELOCITY

CATALYST TYPE

FEEDSTOCK TYPE

CATALYST AGING

TABLE III-3

MAJOR PARAMETERS EXAMINED DURING THE FLUID CATALYTIC CRACKING STUDIES

UNIT PARAMETERS	FEEDSTOCK PARAMETERS
TEMPERATURE	HYDROTREATER CATALYST TYPE
CATALYST TO OIL RATIO	HYDROTREATER SEVERITY
WEIGHT HOURLY SPACE VELOCITY	BASIC NITROGEN CONTENT
UNIT SIZE (SCALE-UP)	BOILING RANGE
	FEEDSTOCK SOURCE OIL
	RECYCLE

processing requirements. Pseudocomponent fractionation and evaluation was also provided in an attempt to define component contributions to the overall crude fuel properties.

Since reformer screening was scheduled for late in the Phase II program, due to the necessity of fully processing samples to that point, a preliminary screening study based on a normal paraffin-doped petroleum turbine fuel was performed early in the program. Results from this screening study were used to define conditions for actual sample processing. Five actual shale samples were processed at estimated required conditions and two samples processed under accelerated aging conditions to examine potential catalyst deactivation rates.

The aromatic saturation studies were performed on the aforementioned reformer samples, including the normal paraffin simulated samples. No aging estimation was made for this unit due to the high quality of the feed and the similarity to conventional processing.

Finally, bottoms product from fluid cracking was processed for recycle. Parameters of feedstock, boiling range, source, temperature and pressure were examined.

All hydrotreating, reforming and aromatic saturation described above were accomplished on 1" nominal trickle flow isothermal laboratory units using once-through hydrogen and off-line stripping. Details of all experimental operations are contained in Volume II (in situ oil) and Volume III (above-ground oil) of this report.

The final element of Task I was definition of chemical process response during extraction. Early in the program, a batch study was performed to evaluate solvent ratios and composition. These results were then used to define required conditions for continuous countercurrent extraction operations. In addition to the above parameters, the continuous extraction experiments evaluated feedstock, temperature and source production parameters. Details are presented in Volumes II and III.

TASK II

Due to relatively severe time constraints on a sequential-product study such as this, the required laboratory samples were prepared concurrent with Task I data generation, and in particular during aging runs where appropriate. Since there is a process option of operating either blocked-out or with concurrent production of all fuels, samples were prepared in both manners for final selection after data acquisition was complete.

COMPUTER MODELING

As early as possible, data were inserted into the computer model initially prepared during Phase I and used for program direction. Due to time considerations, this initial optimization was utilized to define both hydrotreater aging work, as well as recommended Phase III operations.

When all data was in hand, the model was again used with this more complete data set for evaluating two case studies for each oil. Apparent optimum performance and conditions were defined from these results.

SECTION IV

EXPERIMENTAL RESULTS - TASK I

Experimentation was provided under this work area to provide a very wide range of data for eventual computer evaluation. Each portion of work is described below, and detailed data are available in Volumes II and III of this report.

1. Crude Shale Oil Evaluation. Both the in situ and above-ground oils were evaluated as-is and in nominal 100°F pseudocomponents. Table IV-1 presents a comparison of each oil with analogous data for a conventional and an incremental petroleum crude oil.

Both shale oil stocks present lower gravities, and in particular, much lower naphtha content than the conventional petroleum oil. Interestingly enough, the shale materials contain significantly lower sulfur contents, but nitrogen and oxygen levels are several orders of magnitude higher than those found in petroleum. The C/H weight ratio for the in situ oil is 7.3 and the above-ground oil 7.4, which represent relatively high levels of hydrogen content considering both the heteroatom levels and lack of the light (naphtha) fraction. Phenol contents of the shale oils are high compared to the petroleum material, but low relative to other synthetic stocks, and in particular, relative to coal liquids.

TABLE IV-1

CRUDE OIL COMPARISON

ITEM	ARABIAN LIGHT	IN SITU SHALE OIL	ABOVE-GROUND SHALE OIL	MEXICAN MAYA
GRAVITY, °API	33.3	23.6	20.9	22.2
K FACTOR	11.9	11.6	11.4	11.6
SULFUR, WT %	1.8	0.53	0.63	3.4
NITROGEN, WT %	-	1.42	1.85	(>0.31)
BASIC NITROGEN, WT %	(>0.007)	0.86	1.48	(>0.01)
OXYGEN, WT %	-	1.21	1.04	-
POUR POINT, °F	<-20	65	70	<-20
VIS @ 100°F, SUS	46.3	162	205	326
DISSOLVED H_2S, PPM	TR	27	33	14
ORGANIC CHLORIDE, PPM	7.7	4	13	27
BS & W, VOL %	TR	0.1	TR	0.15
SALT, #/1000 BBL	0	2.47	1.98	12.4
CARBON RESIDUE, WT %	-	1.22	1.62	10.2
TOTAL METALS, PPM	(13)	68	106	(340)
ACID NUMBER	-	1.36	1.90	0.24

As reported previously, both by Ashland and others, trace element inclusions are commonly high in shale oils. Iron and nickel, in particular, are commonly encountered as shown. The major metallic contaminant, however, is arsenic, ranging 20 to 40 ppm for these samples. Common occurrence of arsenic in petroleum is in the ppb range or less, and even at those levels can be troublesome. These levels of metallic inclusions have major negative implications to operation of the crude shale oil hydrotreater.

Other contaminants are organic chlorides, dissolved H_2S, BS&W and salt. The levels of these contaminants shown should not be of major negative impact on these materials.

Maleic anhydride value, which is primarily a measure of conjugated diolefins, is high for the shale feedstock. These high values indicate that furnace and heat exchange coking will probably be a problem in the crude shale oil hydrotreater.

Finally, handling properties of the shale oil feedstocks are markedly different from most (though not all) petroleum stocks. High viscosities, and in particular high pour points, dictate that special handling facilities be provided at the refinery. These special facilities are primarily heated tankage and insulated piping. While this does require extra attention by the refiner, it poses no special problem other than recognition of this property of the material.

The key elements delineated above are the increased nitrogen and oxygen contents, and much higher levels of iron and arsenic contaminants, than refiners have been accustomed to handling to date. However, it should be noted that increasing proportional dependence on such crude stocks as Mexican Maya, Venezuelan Heavy and Arabian Heavy are bringing the overall refining feedstock picture closer to the shale oil properties delineated above.

The final major property element of major concern to the refiner when processing shale oil is the boiling range distribution of this material as shown in Figure IV-1. Classic refinery feedstocks produce 10 to 30 volume percent or more of the total crude oil as naphtha (less than about 400°F atmospheric TBP). These shale feedstocks demonstrate 5 volume percent or less of the same fraction. There are advantages to the shale oils in this area, however, as in general there is less residuum (1025°F+) for shale oils and in specific essentially no residuum for the in situ material. The residuum fraction is of relatively low value (in general less than the cost of the crude itself) and normally very difficult and/or expensive to process. Further, the relatively heavy, new petroleum crudes now becoming available (referred to above) also are showing much lower naphtha yields, similar to that encountered with the shale oils. Of primary importance, however, is that these crudes are also increasing in residuum content, and as such may actually be poorer refinery feedstocks than shale oils.

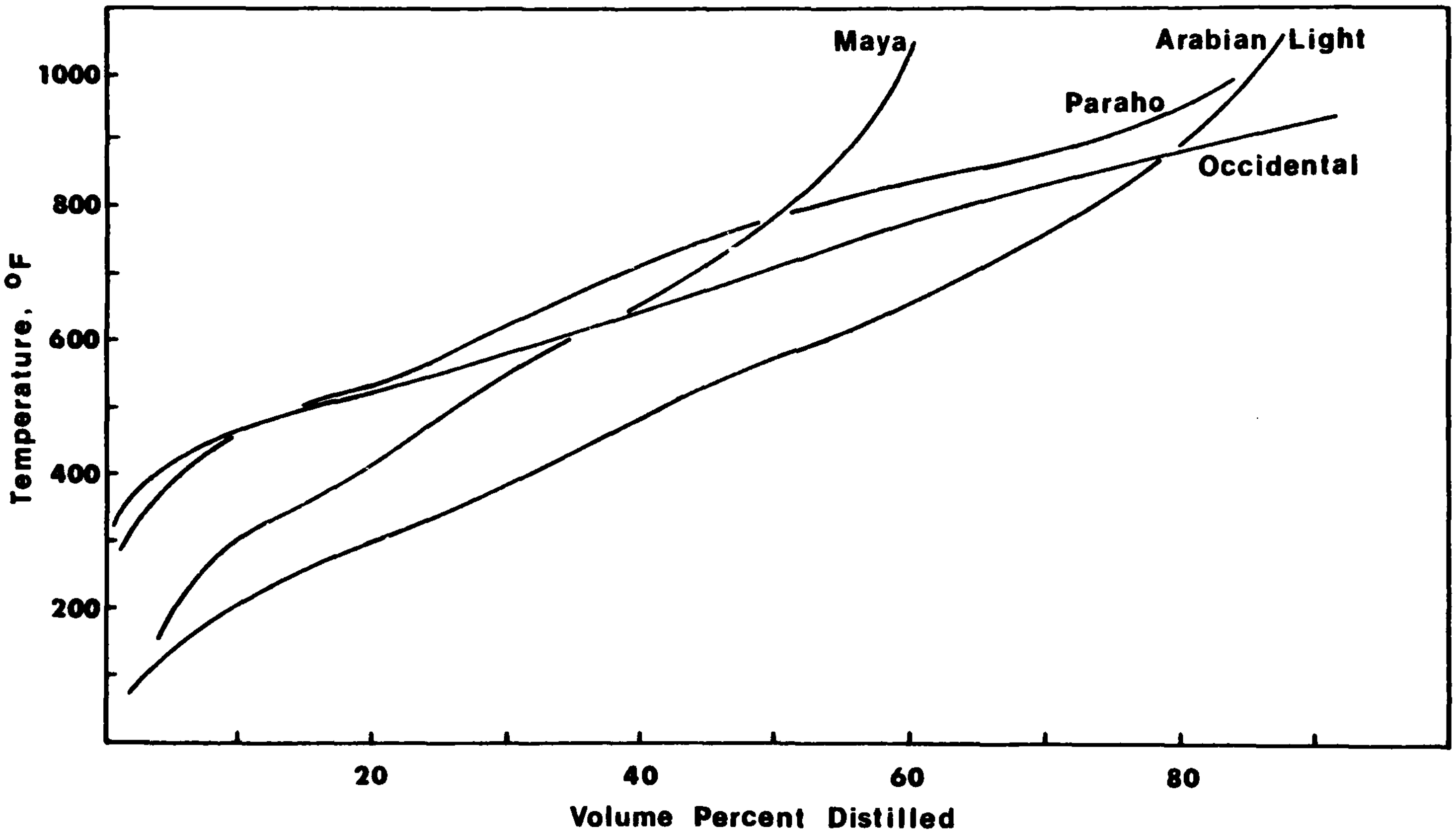

Figure IV-1. Comparative Boiling Range Distribution

The final relative value of each material, however, is strictly refinery and, in particular, equipment and market dependent.

In conclusion, these shale oil feedstocks do, in fact, present the refining problems postulated a priori:

- Heteroatom content, particularly oxygen and nitrogen
- Arsenic and metallic contaminants
- High normal paraffin content (low fluidity)
- High conjugated diolefin levels
- Boiling range distribution significantly different from present refinery feedstocks

There are two key relative evaluations of these materials necessary in light of these properties. First, the refiner must evaluate these feedstocks in terms of his historical refinery runs. In that light, shale oils are poor competition with the conventional petroleum materials and, in all probability, require additional capital investment to existing refineries. However, a second aspect must be considered as well, which may be of even more significance. Present crude oil supplies are limited, and in many cases incremental refinery feedstocks are limited to the heavier crude grades. Often these crudes are comparable and sometimes even inferior to the shale oil feedstocks. Therefore, on an incremental feedstocks basis, these shale oils may even be competitive with present poorer grades of petroleum crude oils.

Finally, attainment of significant throughputs of either shale oils or incremental petroleum stocks, while producing conventional product slates, will require additional capital investment to most, if not all, existing refineries. While this program addresses essentially new refinery construction, the process developed herein is adaptable as well to existing sour crude refineries at relatively modest investment. In fact, under optimum processing conditions when using the EXTRACTACRACKING process in a modified existing refinery, there are (as yet unproven) indicators that these shale oils could be more profitable to process than the heavy incremental petroleum feedstocks discussed above. An example of potential existing refinery modifications to use shale oil via EXTRACTACRACKING is shown in Figure IV-2.

2. Crude Shale Oil Hydrotreating. Crude shale oil hydrotreating is a key element in the EXTRACTACRACKING process, but in a different manner from most previous work in this field. The great majority of previous experimental work on hydrotreatment of crude shale oil has been centered on high severity upgrading to petroleum quality. In particular, hydrotreating at those severities produces a material probably superior to most crude oils, in particular for fluid catalytic cracking work. The present definitive work in this area was accomplished by Chevron(3), while

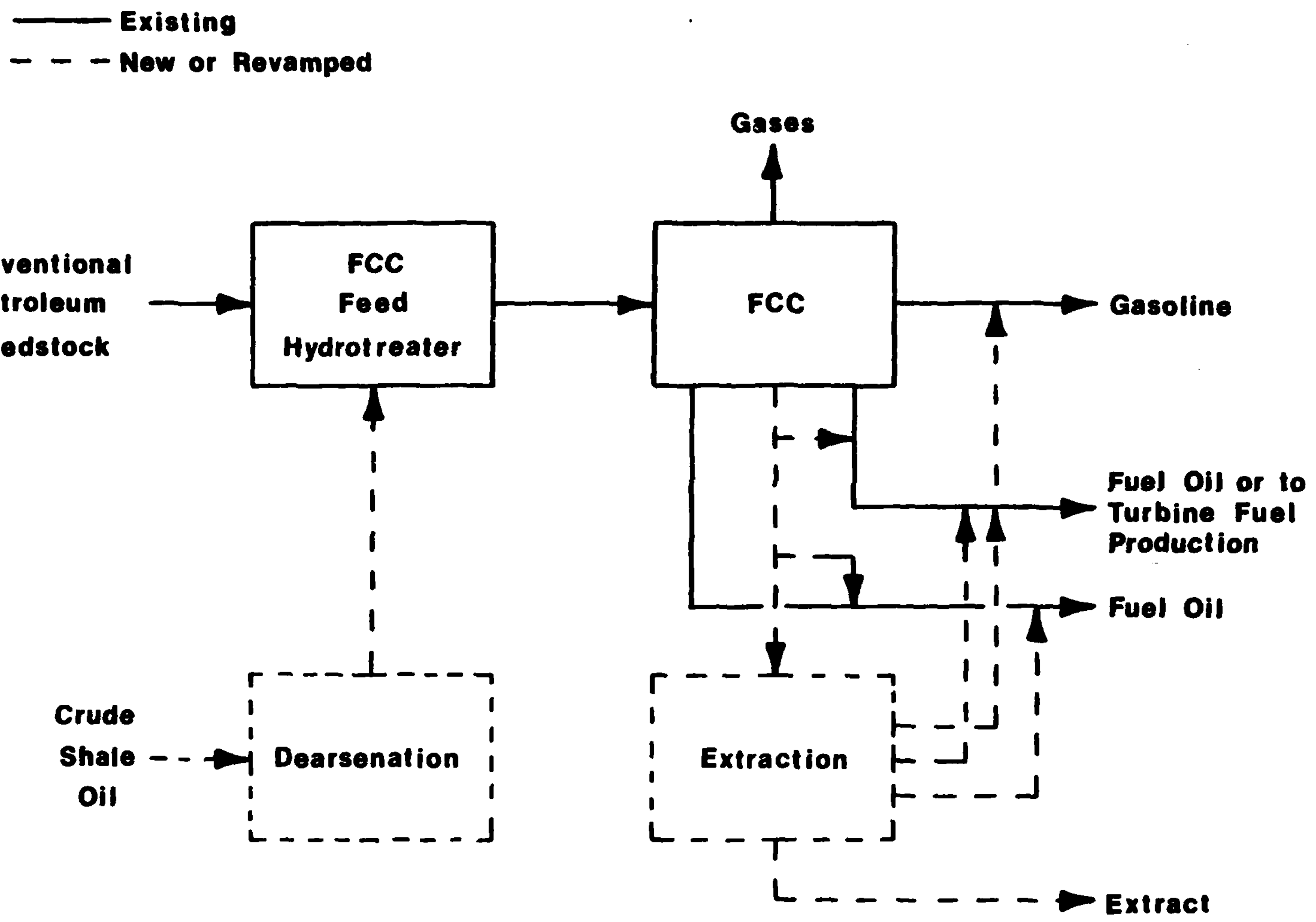

Figure IV-2. An Example Of Integrating EXTRACTACRACKING®
With An Existing Petroleum Refinery

processing Paraho Oil, with other studies by Exxon(1) for both in situ and above-ground oils also pertinent to these results.

A key factor in evaluating the EXTRACTACRACKING results, to be kept in mind when comparing these results to those of other studies, is that the catalysts used in these studies were selected for their low severity activity. There are other catalysts available which will show improved results under higher severity operations.

In particular, the severities desired for use in this module correspond to present commercial vacuum gas oil technology or lower. If successful, limitation of the operating severity to this level has the advantages of: (1) being commercially proven, (2) being compatible with refining operations presently available and (3) being a least-cost option, both in operating and capital terms. A key element to remember is that, due to throughput and other factors, total hydrogen consumption is defined for all practical purposes in this plant section.

As noted previously, three study sets were provided for each oil: parameter variation, during which operating conditions and catalysts were evaluated; 5-day studies, in which two catalysts were evaluated for stability; and aging studies for a selected catalyst. In this section the response of each oil will be discussed separately and then compared. An overview of objectives and key features for this module is shown in Table IV-2.

TABLE IV-2

CRUDE SHALE OIL HYDROTREATER

Objectives:	Provide olefin saturation, metals removal, and desulfurization at minimum denitrogenation, hydrogen consumption, and operating severity
Key Element:	Hydrogen consumption
Parameters Evaluated:	• Operating severity • Catalyst type • Shale oil type
Unique Features:	• Low pressure operation • Operating parameters corresponding to present commercial practice

IN SITU OIL

A total of 72 data points were derived under the parameter variation studies on in situ oil. Details of these data are presented in Volume II, with only the highlights discussed here.

The key element of interest in the crude shale oil hydrotreater is hydrogen consumption and, in particular, the efficiency of hydrogen consumption. As expected, at the milder conditions evaluated, total hydrogen consumption increased rapidly with increasing system (and therefore hydrogen) pressure. Figure IV-3 demonstrates these trends. There are two schools of thought regarding this functionality. First, typified by previous work, the increased hydrogen consumption is viewed as beneficial. This analysis is, in fact, probably true for conventional types of processing. However, the second school of thought, which we are developing herein, focuses on a different aspect. We wish to minimize total hydrogen consumption at this stage of the process, while producing a feedstock of minimum acceptable quality to the downstream modules. Thus, at least conceptually, the conventional types of refining would be located in the upper right-hand corner of this plot, and new types of processes such as EXTRACTACRACKING in the lower left-hand region.

Figure IV-4 expands this point further. For conventional processing, high temperatures (700°F or greater) are required to reduce nitrogen content to relatively low

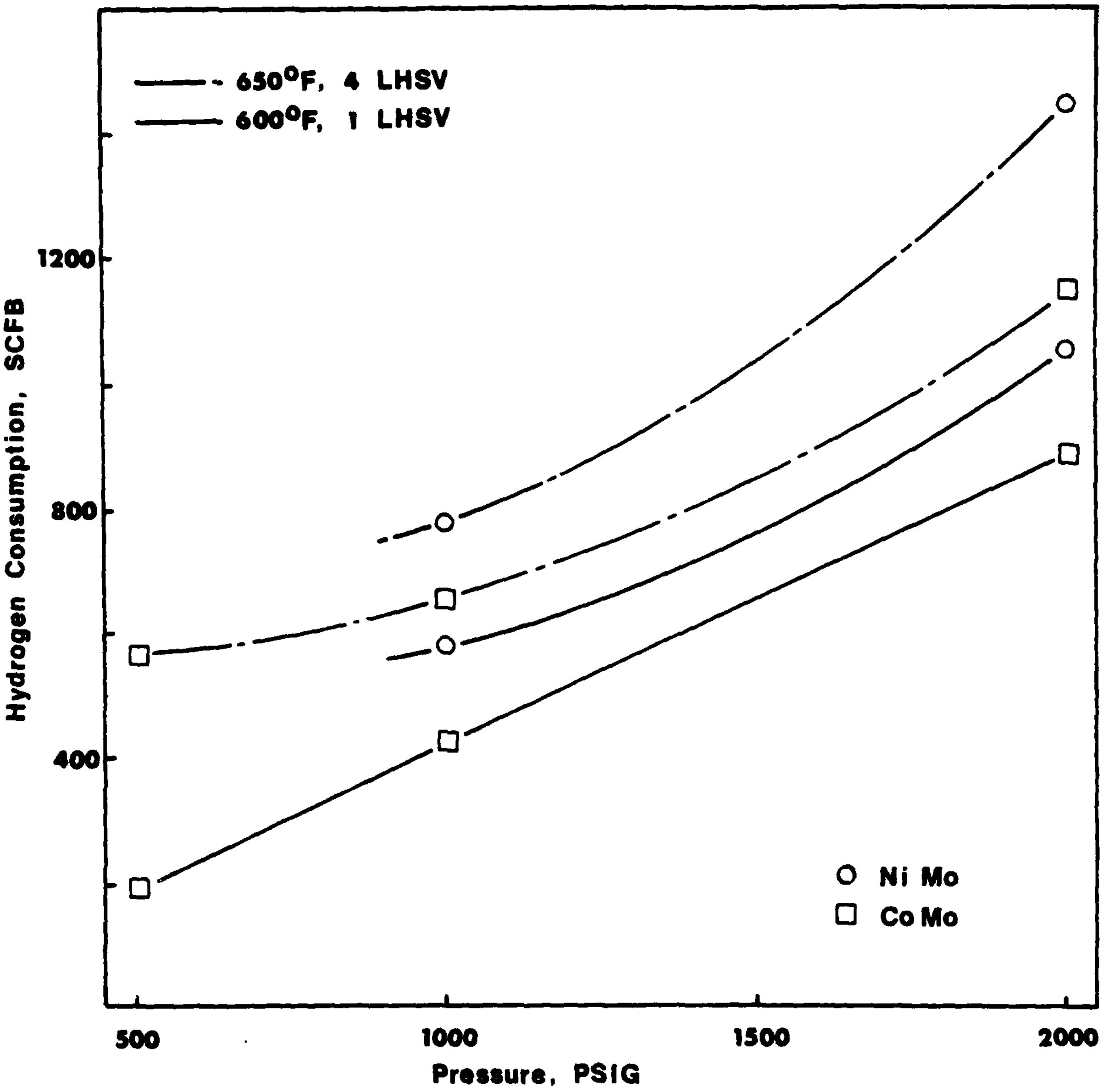

Figure IV-3. Hydrogen Consumption Trends

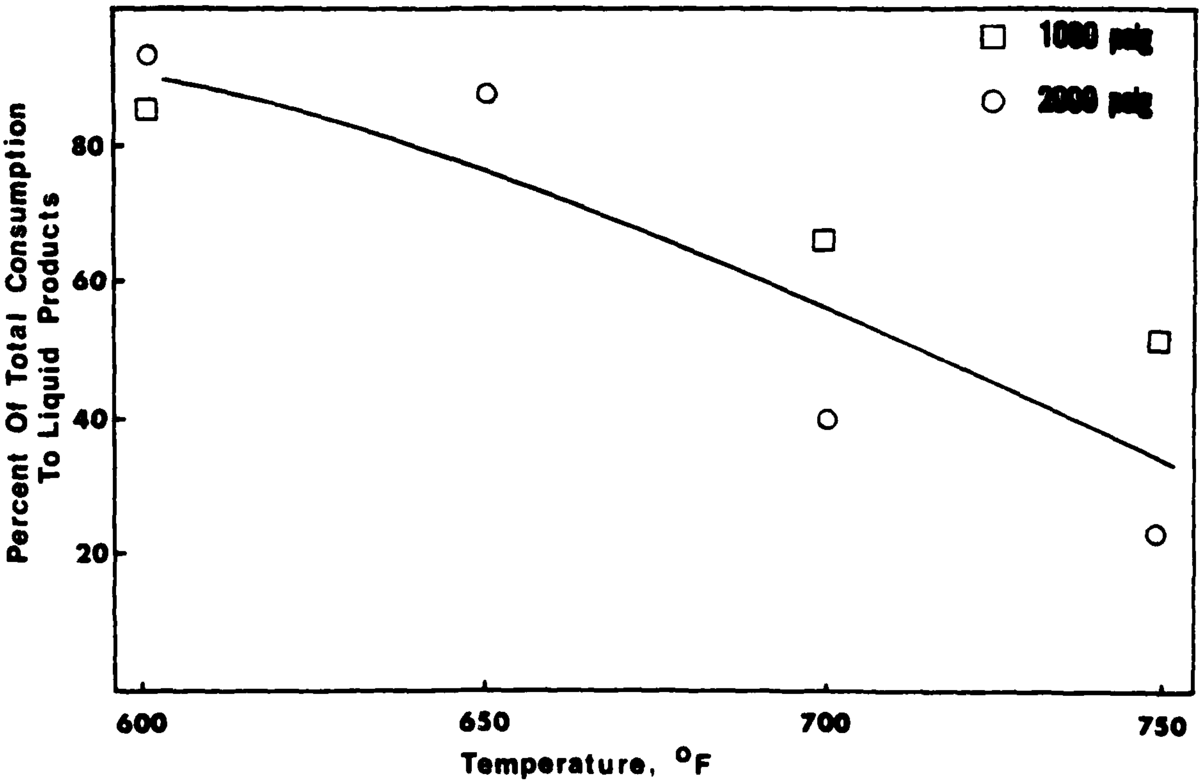

Figure IV-4. Hydrogen Consumption Efficiency levels. This higher temperature also implies at least some degree of hydrocracking activity in the unit, leading directly to the plot in Figure IV-4. For all pressures, the efficiency of hydrogen utilization (expressed as percent of total consumption, representing an increase in hydrogen content of the liquid) decreases with increasing temperature. Of even more importance, as the reaction temperature approaches 700°F, the degree of hydrocracking increases rapidly, causing a marked decrease in utilization efficiency when operating at 2000 psig. Further, while operations at 1000 psig show the same general trend, the decrease in efficiency as temperature increases is not as great. The high efficiencies realized at 600°F under all pressures are intriguing in particular, although actual plant requirements may not allow operations at this low temperature. There may be definite advantages to operations at the highest pressure and lowest temperature, although the rapid increase in capital cost and operating problems at those conditions prevent simple analysis of this operation. This alternative, however, will be considered during Phase IV.

The final key operating condition for this unit is space velocity (alternatively throughput or residence time). Selected data are plotted in Figure IV-5, again against hydrogen utilization efficiency. There is a moderate scatter of the data, but in particular, the range of

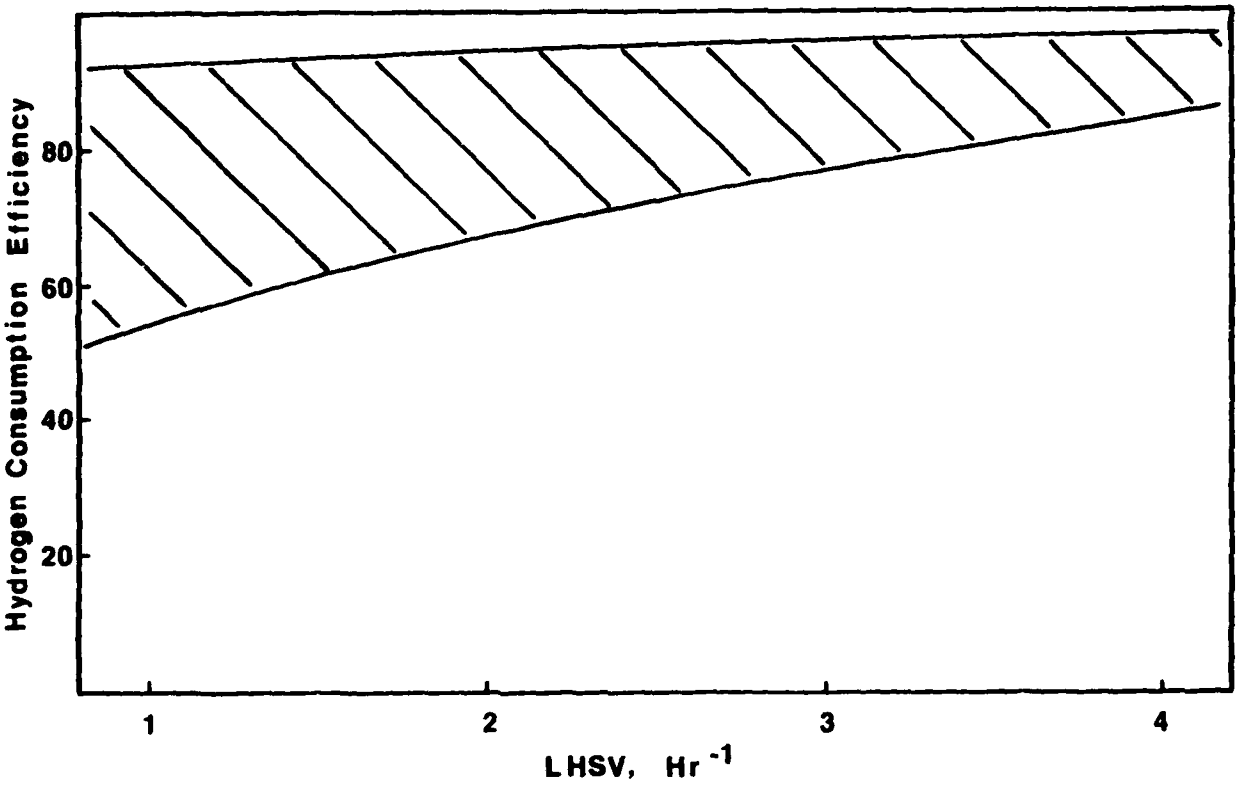

Figure IV-5. Efficiency Of Hydrogen Consumption As A Function Of Space Velocity efficiency tends to decrease with increasing space velocity, and the overall trend is to increase efficiency with increasing space velocity. This result is reasonable in plant experience terms, as the resulting decrease in residence time should decrease the by-product gas production reactions as shown. Providing increased throughput for efficiency considerations also has a further advantage in reducing the required size, and therefore capital cost, of the unit. (The high hydrogen utilization efficiency at low temperature and high pressure is again demonstrated in this graph.)

Overall, with the objective of minimizing total hydrogen consumption while maximizing utilization efficiency, the data indicate that low temperature, high space velocity regions are favored. The complex pressure functionality is somewhat indeterminate, although there may be advantages to the higher pressures at the lowest (<650°F) temperature ranges. Subjectively, the moderate pressure region appears to be favored at intermediate (650-700°F) temperatures.

Both cobalt molybdate and nickel molybdate catalysts in general show agreeing trends, although there is somewhat more scatter to the data for the nickel molybdate catalyst. Further, the 650°F data at all pressures seem to be anomolous; whether this is in fact true or is some unexplained phenomena occurring is unclear at present. At a given (comparable) set of conditions, hydrogen consumption tends to be higher for the nickel molybdate catalyst than the cobalt molybdate (Figure IV-3). Hydrogen utilization efficiency appears to be comparable in terms of temperature functionality, while the scatter in terms of space velocity relationships for the nickel molybdate data prevents a rational comparison. Overall, the cobalt molybdate catalyst appears to be favored on a hydrogen consumption basis due to comparable utilization efficiencies and lower total hydrogen consumption.

Of key interest in many studies is the degree and/or relative rate of heteroatom removal. While of secondary interest here, the relationships between heteroatom removal and required operating severity are important for further processing modules. Both desulfurization and denitrogenation were fitted by second order kinetic expressions of the form:

$$\frac{1}{C} - \frac{1}{C_o} = K_o \text{ EXP } \left(- \frac{E}{RT} \right) PA/(LHSV)$$

Where C = heteroatom concentration (wt %) in the liquid
C_o = heteroatom concentration in the feed
K_o = rate constant
E = activation energy
R = gas constant, 1.987 Btu/lb-mole. °R
T = temperature (°R)
P = pressure (psia)
A = pressure exponent, a constant
LHSV = liquid hourly space velocity

The desulfurization data show several distinct trends. First, there is a distinct positive effect of pressure for the range 500 to 1000 psig for both catalysts, but no significant pressure factor for the 1000 to 2000 psig range. The zero pressure exponent is consistent with theoretical desulfurization mechanisms, while the low pressure exponents are probably due to mass transfer limitations in that system. Based on the zero pressure exponent analysis, the nickel molybdate catalyst presents the highest desulfurization rates of the two catalyst systems. Based on these models, the cobalt molybdate provides a 0.82 relative activity (based on nickel molybdate = 1.0) at 650°F. For desulfurization equivalent to the cobalt molybdate results at 650°F, the nickel molybdate catalyst temperature requirement is 640°F or a 10°F advantage at 1000 psig and 2 LHSV. However, at these conditions the cobalt molybdate system requires approximately 100 SCFB less hydrogen. Figure IV-6 presents a comparison of these data.

For denitrogenation, pressure exponents for both catalysts were non-zero and positive. This, again, is in agreement with theoretical considerations. For both catalysts, there is again an increased pressure dependence in the 500 to 1000 psig range, probably due to the aforementioned mass transfer limitations. The nickel molybdate catalyst results have a much lower apparent pressure dependence than the cobalt molydate, which is somewhat surprising. The Co/Mo results are second order in pressure, while the Ni/Mo data

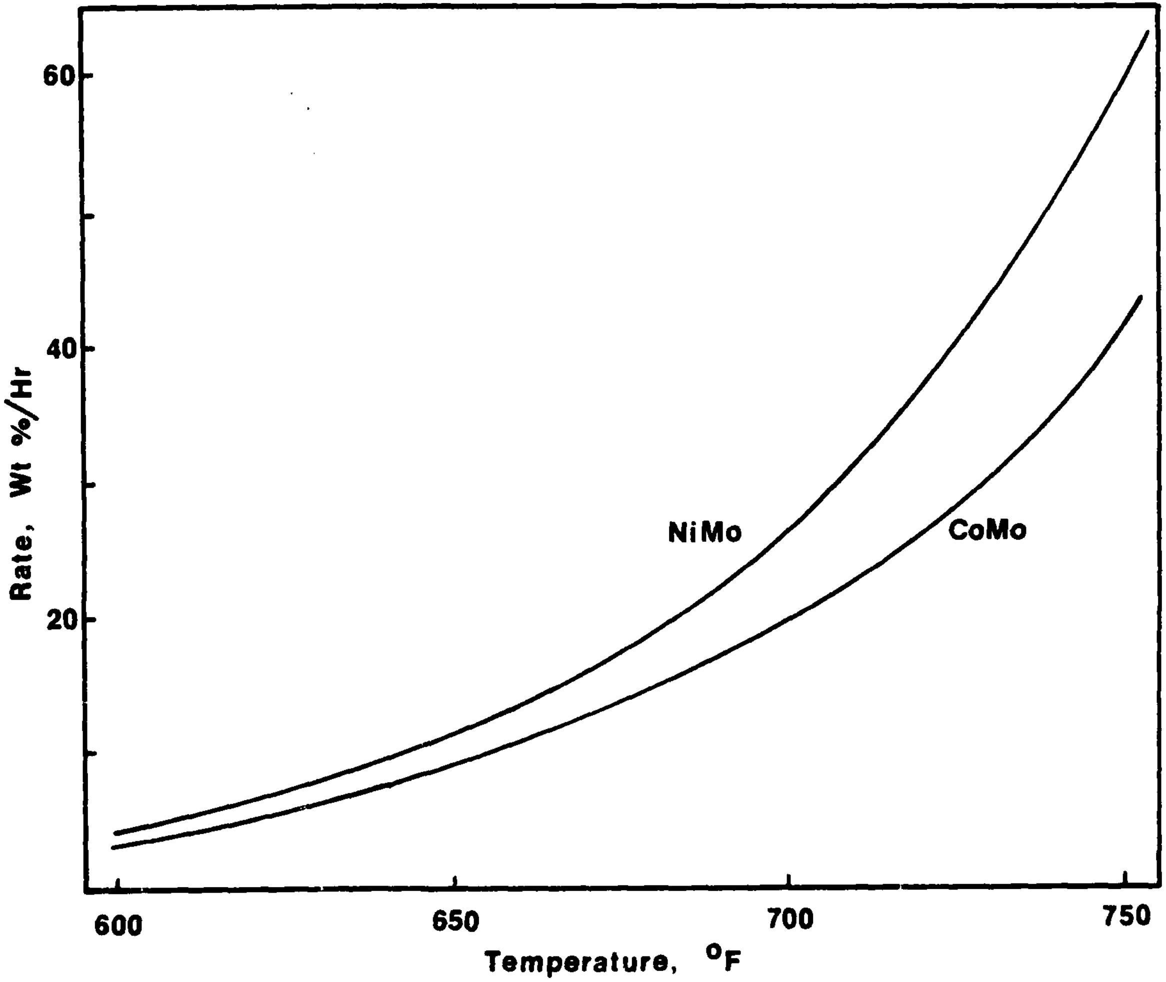

Figure IV-6. Comparative Desulfurization Rates For In Situ Oil are essentially first order. Further, there was less total response difference between the 500 to 1000 and 1000 to 2000 psig nickel molybdate data.

As with the sulfur model, the nitrogen data show the nickel molybdate to have both a higher activation energy, as well as rate constant, with the overall rate for the temperature range of interest, again higher for the Ni/Mo catalyst (Figure IV-7) at all conditions except the 600-675°F range at 2000 psig. For the denitrogenation obtained over cobalt molybdate at 650°F, 1000 psig and 2 LHSV, a temperature of 620°F would be required at equivalent pressure and space velocity over the nickel molybdate catalyst. Relative activity of the Co/Mo catalyst is 51 percent at 650°F and 1000 psig, but 112 percent at 650°F and 2000 psig.

Overall, in terms of heteroatom removal, the nickel molybdate catalyst is favored. At conditions of 1000 psig and 2 LHSV, this catalyst presents 10°F and 30°F temperature advantages for desulfurization and denitrogenation, respectively, over the cobalt molybdate at 650°F. Even at these comparable conditions, however, the nickel molybdate provides a slightly higher hydrogen consumption, probably due to the increased aromatic saturation activity of this catalyst.

The final key element of this analysis for present purposes is the relationship of product/feedstock basic versus total nitrogen. Due to the nature of this process, high ratios of basic to total nitrogen are (predicted to

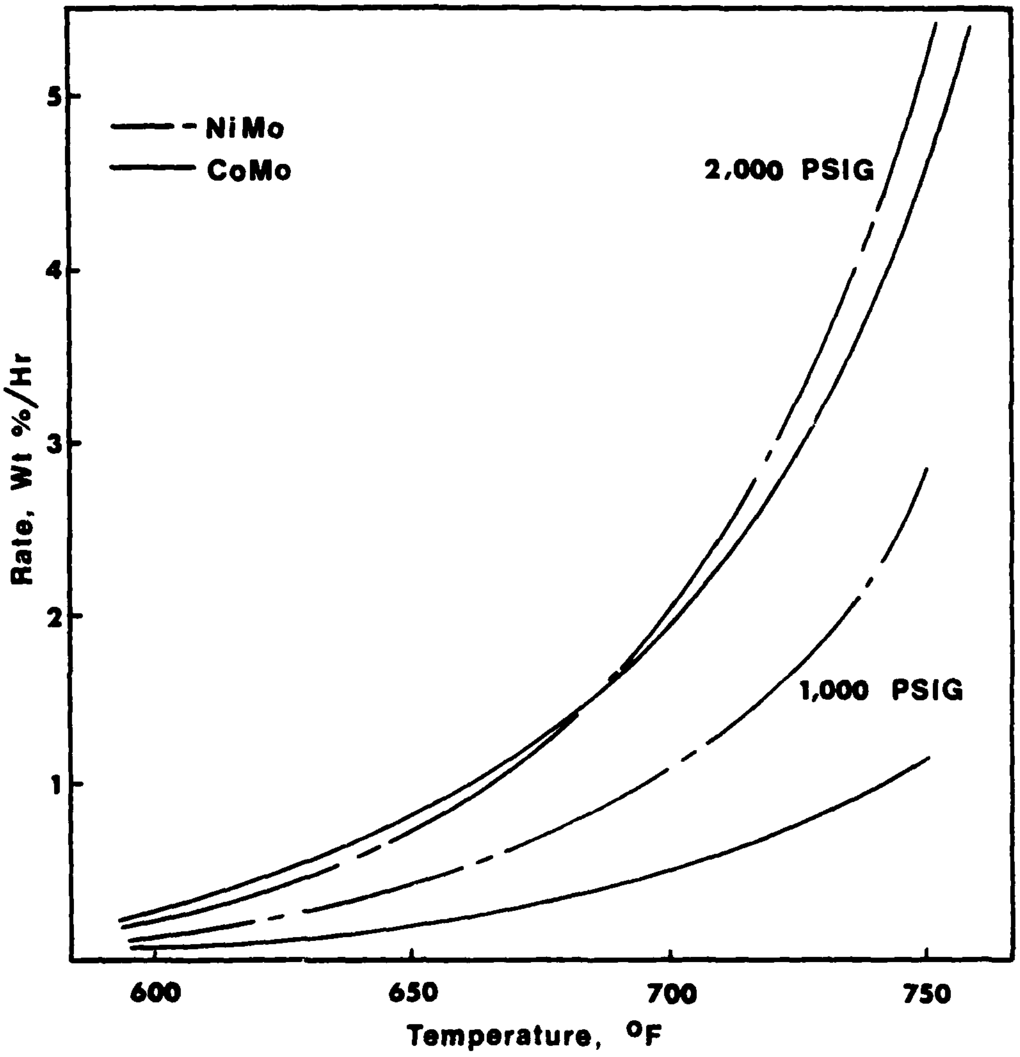

Figure IV-7. Comparative Denitrogenation Rates For In Situ Oil be) desirable in the -600°F distillate, while the opposite is true for the gas oil (+600°F) stream. In general, as shown in Figures IV-8, the ratio:

basic nitrogen : total nitrogen/product - basic nitrogen : total nitrogen/feed

tends to reach a maximum in the region of 650°F for essentially all test data available. Further, the maximum ratio attained for the distillate (400 to 600°F) fraction, which is of primary importance, appears to decrease with increasing pressure. And finally, the maximum ratio attained by the cobalt molybdate distillate product appears to be greater than that produced by the nickel molybdate material. These data have not been completely evaluated, and in some cases are not definitive, but overall consideration of the resulting basic : total nitrogen ratio seems to indicate that the cobalt molybdate catalyst produces a higher level of basic nitrogen relative to total nitrogen than the nickel molybdate catalyst.

In order to examine initial stabilized catalyst activity, single condition, nominal 100 hour runs, were provided for both these catalysts with in situ oil. As shown in Figures IV-9 and IV-10, and in Volume II, a total of 70 hours was required to reach apparent catalyst equilibrium. The dashed lines show predicted start-of-run heteroatom removal levels based on the parameter screening data. For both runs, adequate agreement on lined-out desulfurization

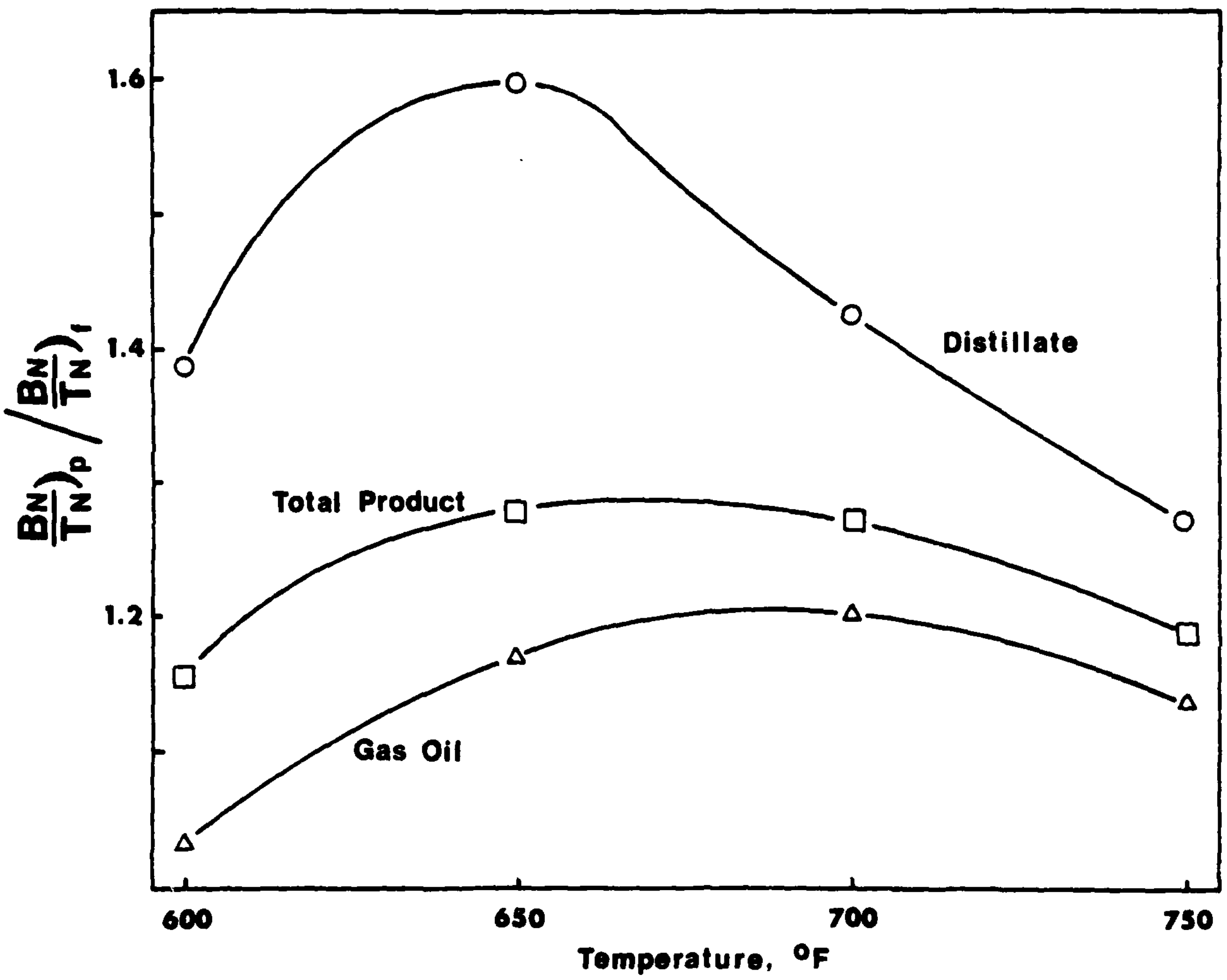

Figure IV-8. Basic Nitrogen Generation

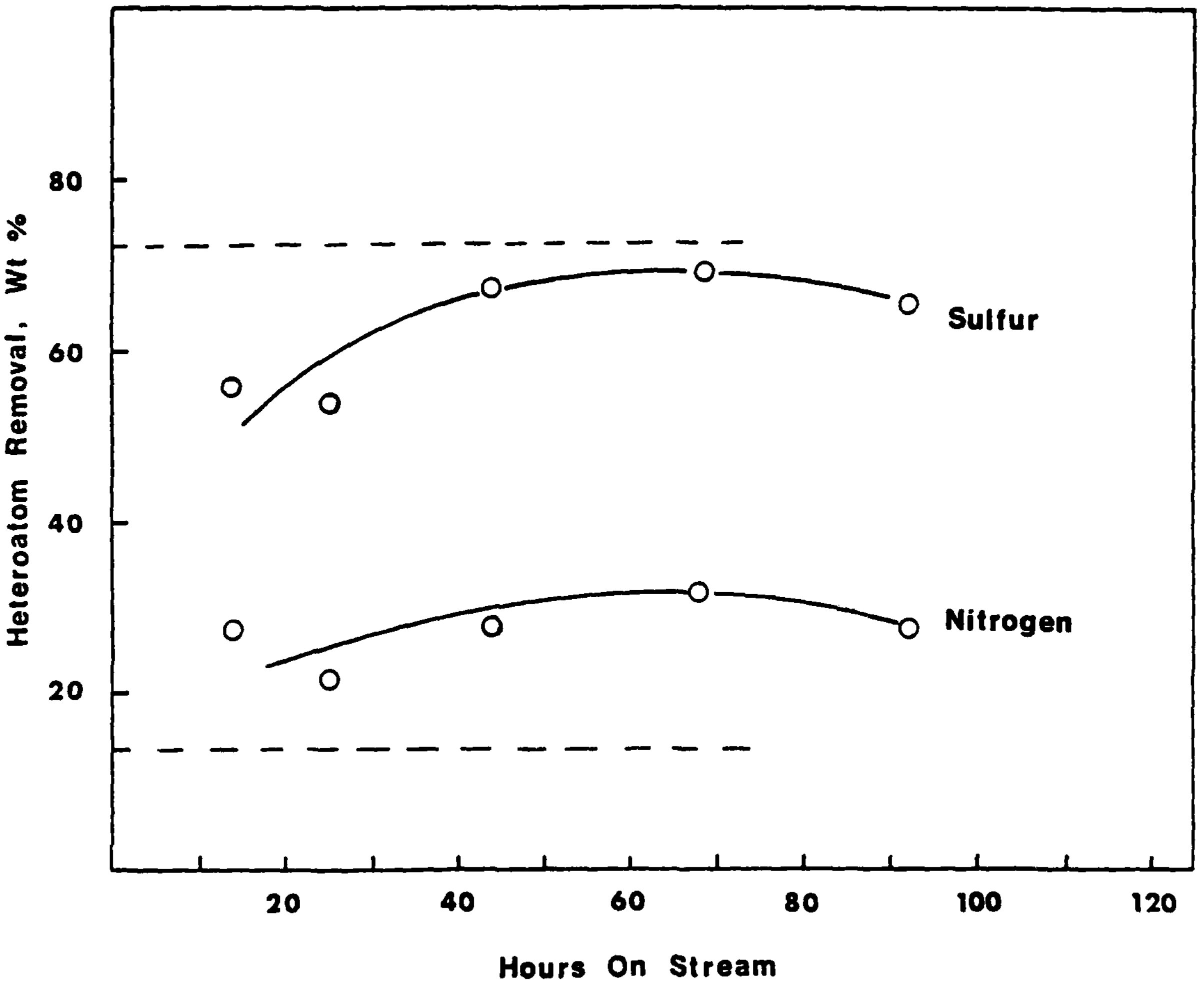

Figure IV-9. Heteroatom Removal Stability - Crude Shale Oil Hydrotreating - Series M-11

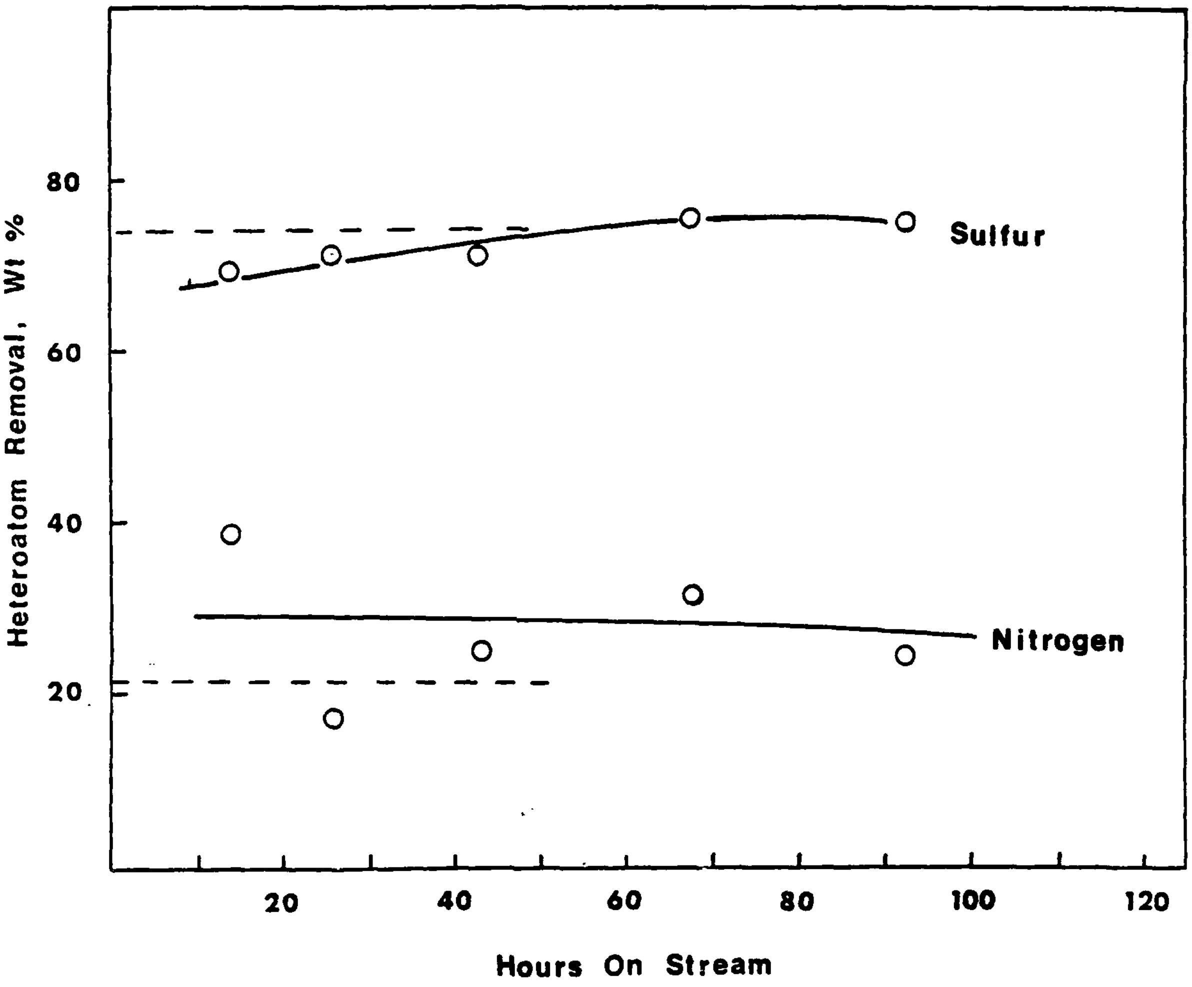

Figure IV-10. Heteroatom Removal Stability – Crude Shale Oil Hydrotreating – Series M-12 is attained, but denitrogenation activity is understated significantly in both cases. There is no good explanation for this phenomenon, other than the aforementioned extensive lineout time required for apparent catalyst equilibration.

Based on these results, there appears to be only a small degree of difference between the two catalysts at mild conditions. Based on target objectives of minimal hydrogen consumption, maximized hydrogen utilization efficiency, minimum denitrogenation and maximum basic nitrogen: total nitrogen ratios in the distillate, the cobalt molybdate catalyst was selected for evaluation of initial catalyst stability parameters. Preliminary process evaluation at this time also indicated that slightly higher severity was desirable in this hydrotreater when using cobalt molybdate catalyst.

Conditions for this catalyst stability run are shown in Figure IV-11 as a function of time on stream. Temperature control during the run was good, but, due to several pump and guardbed problems, both pressure and flow control were somewhat erratic.

Overall, results from the run were reasonably stable (Figure IV-11 & 12). Hydrogen consumption appeared to stabilize in the 600 to 700 SCFB range after about period 7 (160 hours on stream), except for periods 21 to 24 where operating problems caused highly fluctuating results.

Sulfur data were both erratic and disappointing. Analyses of these data after completion of the run indicated

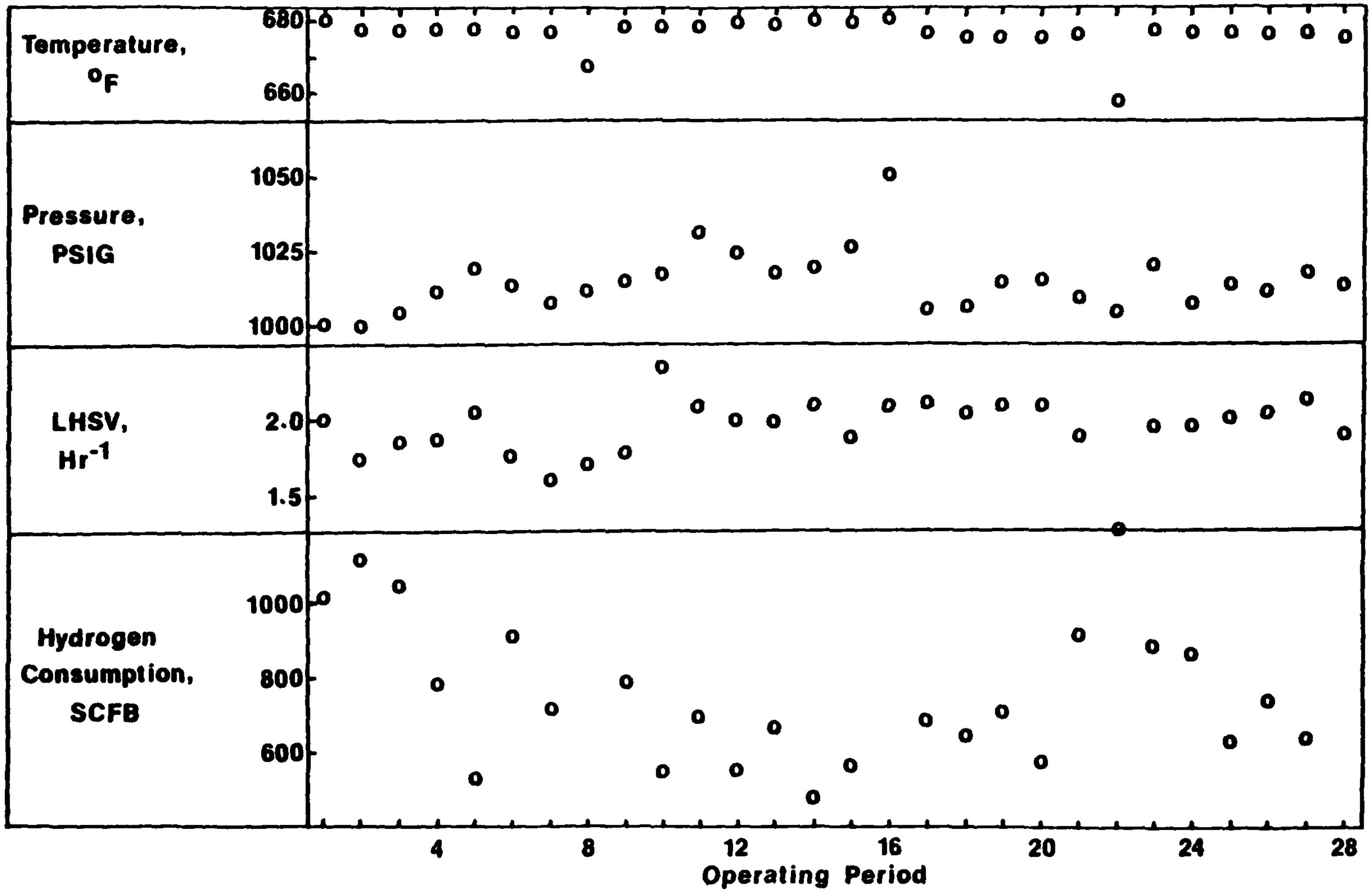

Figure IV-11. CSHT Aging Results For In Situ Shale Oil

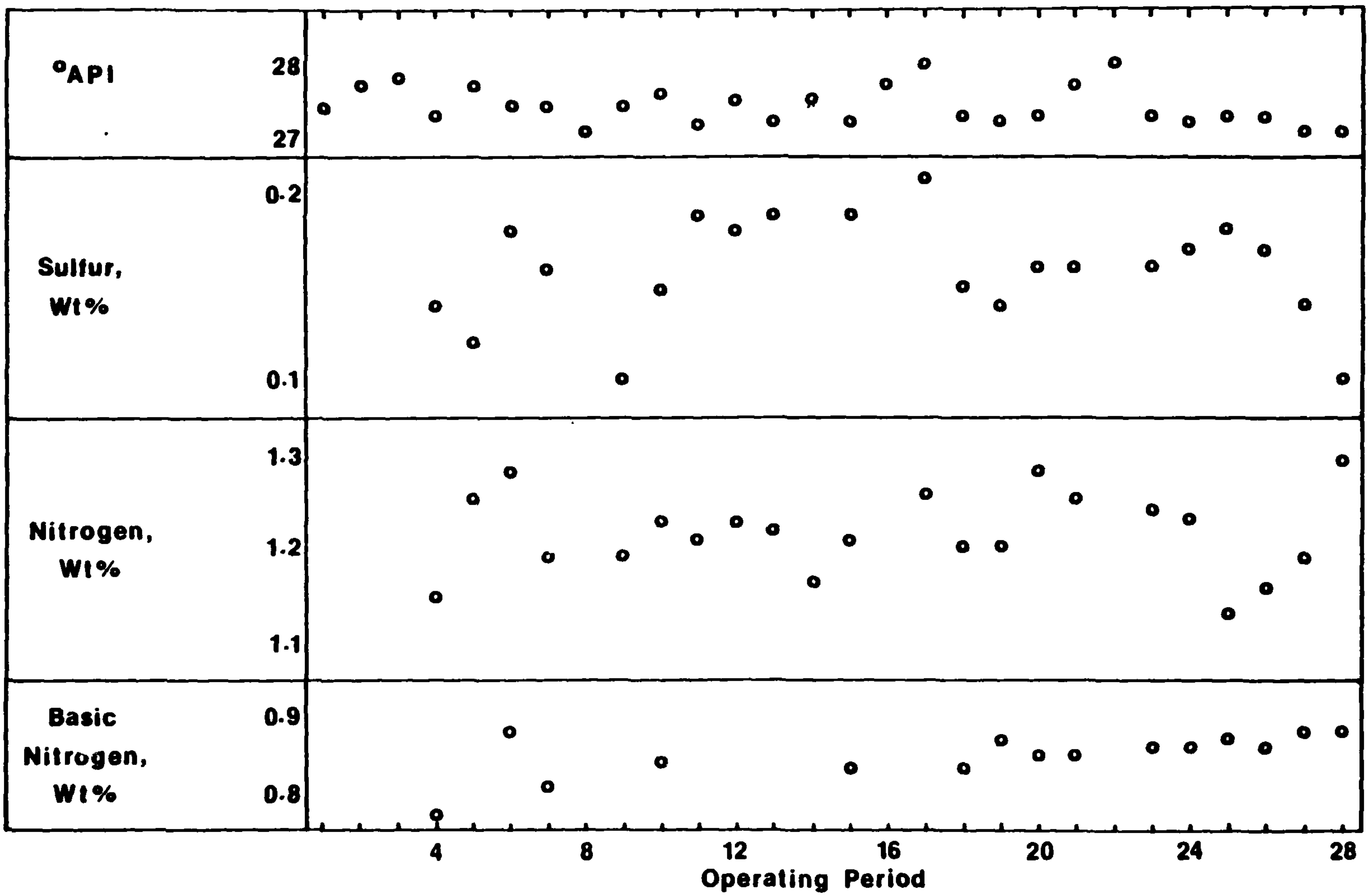

Figure IV-12. CSHT Aging Results For In Situ Shale Oil poor H_2S removal in the stripping operation. Examination of the fractionated product results (see Volume II) confirmed this problem, with actual sulfur levels in the 0.12 to 0.14 weight percent range. The parameter variation data predicted a product sulfur of 0.12 weight percent for excellent agreement with the fractionated results.

Nitrogen results presented a fairly large degree of scatter, but in general demonstrated a good degree of stability. Linear fit of these data denote essentially zero loss of denitrogenation activity after 28 days on stream. Start-of-run product nitrogen level of 1.22 weight percent (obtained by zero ordinate evaluation from the linear fit above) was slightly higher than predicted by the parameter variation model (1.16), but basically in agreement.

Product basic nitrogen presented a very consistent increase, from a (calculated) 0.80 level initially (time = 0) to 0.88 at day 30. In combination with the (calculated) stable product nitrogen level, this trend indicates that, as this catalyst ages, the relative ratio of basic nitrogen compounds in the product liquid increases.

Overall, these results demonstrate that commercially acceptable run lengths (greater than 6 months, and probably greater than 1 year) can be achieved under these conditions. Further, the aged catalyst may well produce better relative basic nitrogen results than the fresh catalyst charge.

ABOVE-GROUND OIL

Eighteen parameter variation data points were evaluated for the above-ground oil. Details of these studies are presented in Volume III of this report.

Detailed hydrogen distribution response was not developed for this material due to the limited number of data points, but, in general, the trends developed for the in situ oil hold for the above-ground as well. Relatively high hydrogen consumptions were encountered during all runs.

As shown in Figure IV-13, desulfurization was high for all conditions and catalysts evaluated. As expected, however, the cobalt molybdate catalyst provided significantly higher desulfurization rates at the lower severities than the nickel molybdate. In general, desulfurization rates were best fitted by second order kinetic plots.

Again, in accordance with expectations, the nickel molybdate catalyst provided higher denitrogenation rates than the cobalt molybdate at comparable conditions (Figure IV-14). A more graphical portrayal of this behavior is also shown in Figure IV-15, demonstrating the relation between desulfurization and denitrogenation for the two catalysts. As in the case of desulfurization data, denitrogenation was best fitted kinetically by a second order model.

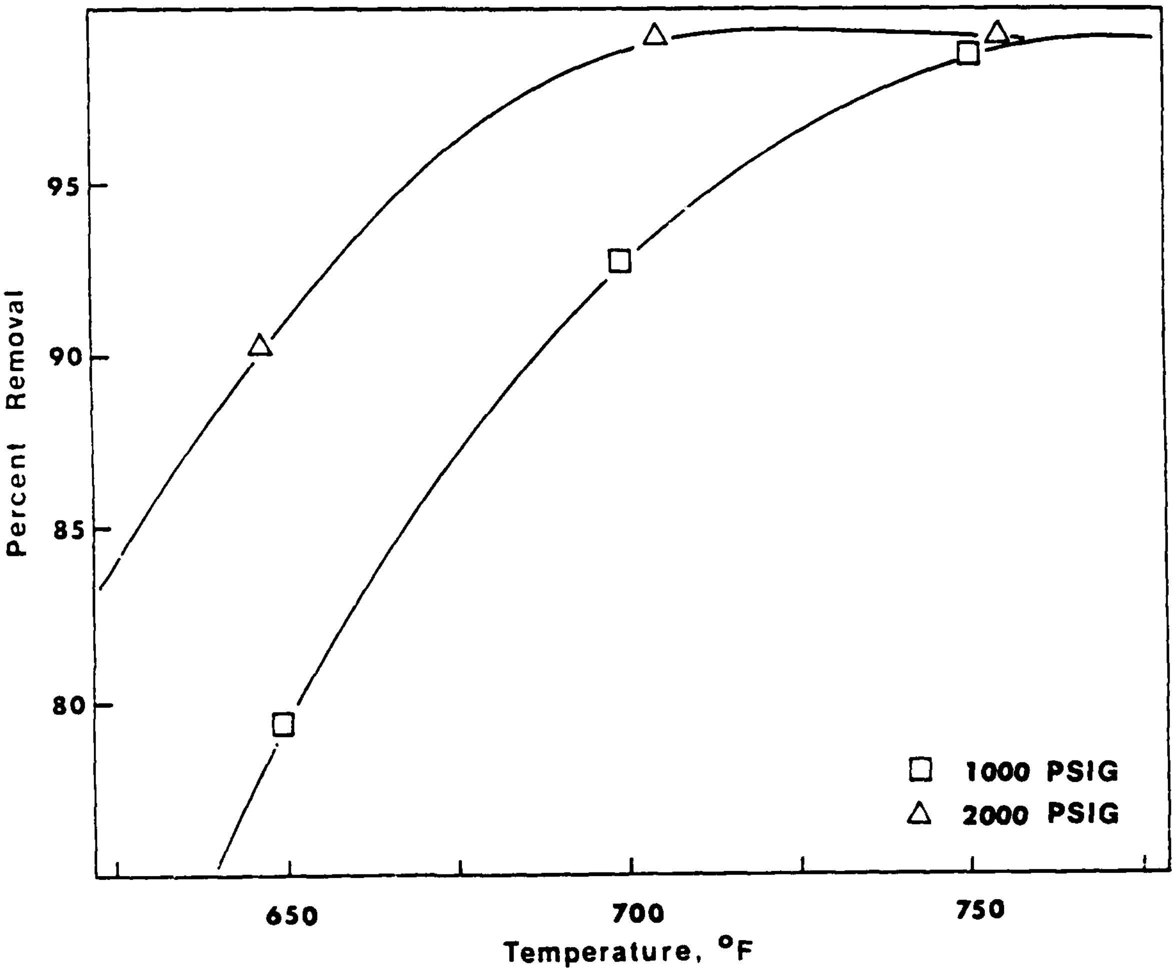

Figure IV-13. Temperature Dependence Of Desulfurization At 2 LHSV On Co/Mo

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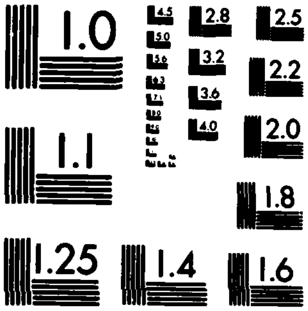
PART II PREPARATIO..(U) ASHLAND PETROLEUM CO KY
H F MOORE MAR 82 AFWAL-TR-81-2056-VOL-1-PT-2
UNCLASSIFIED F33615-78-C-2080 F/G 21/4 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

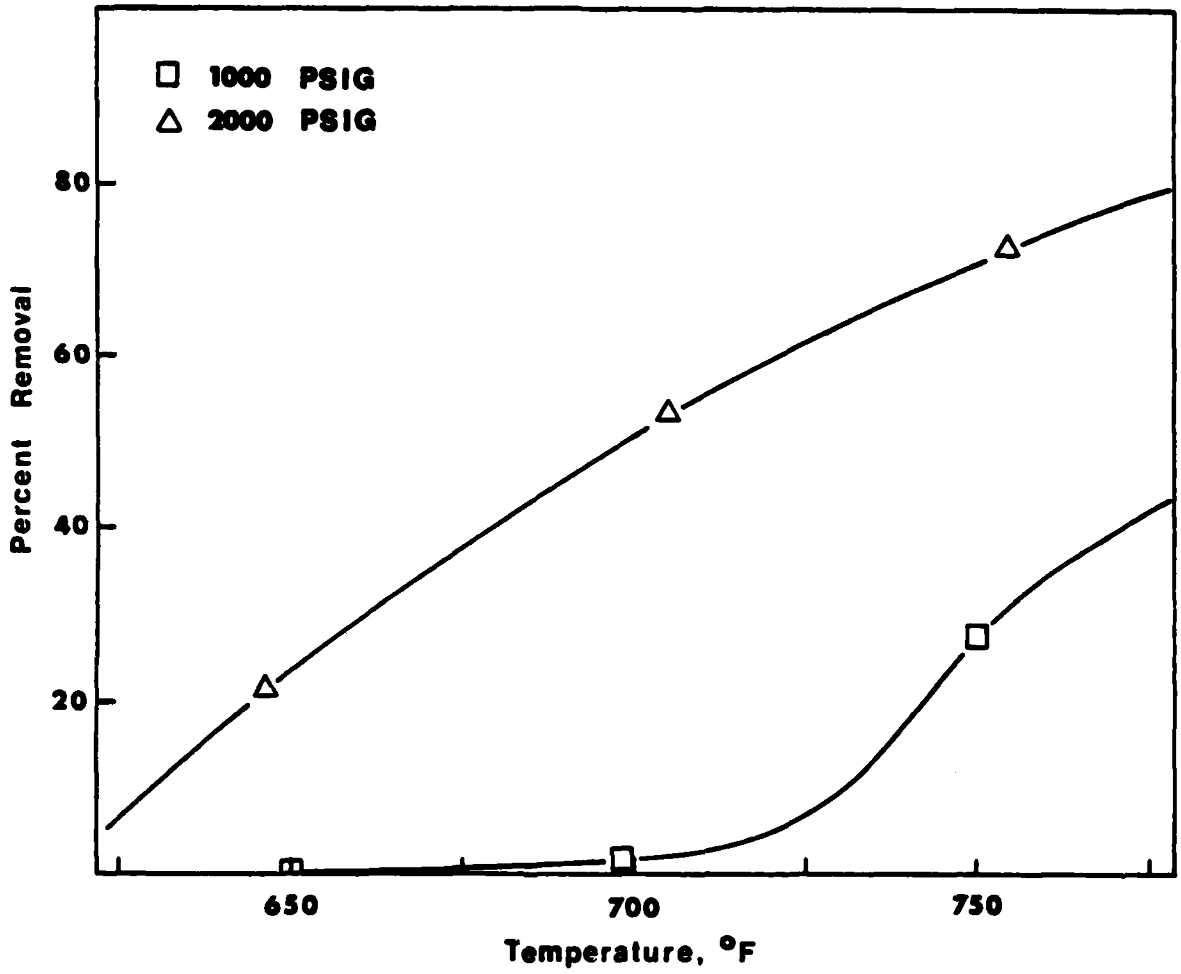


Figure IV-14. Temperature Dependence Of Denitrogenation At 2 LHSV On Co/Mo

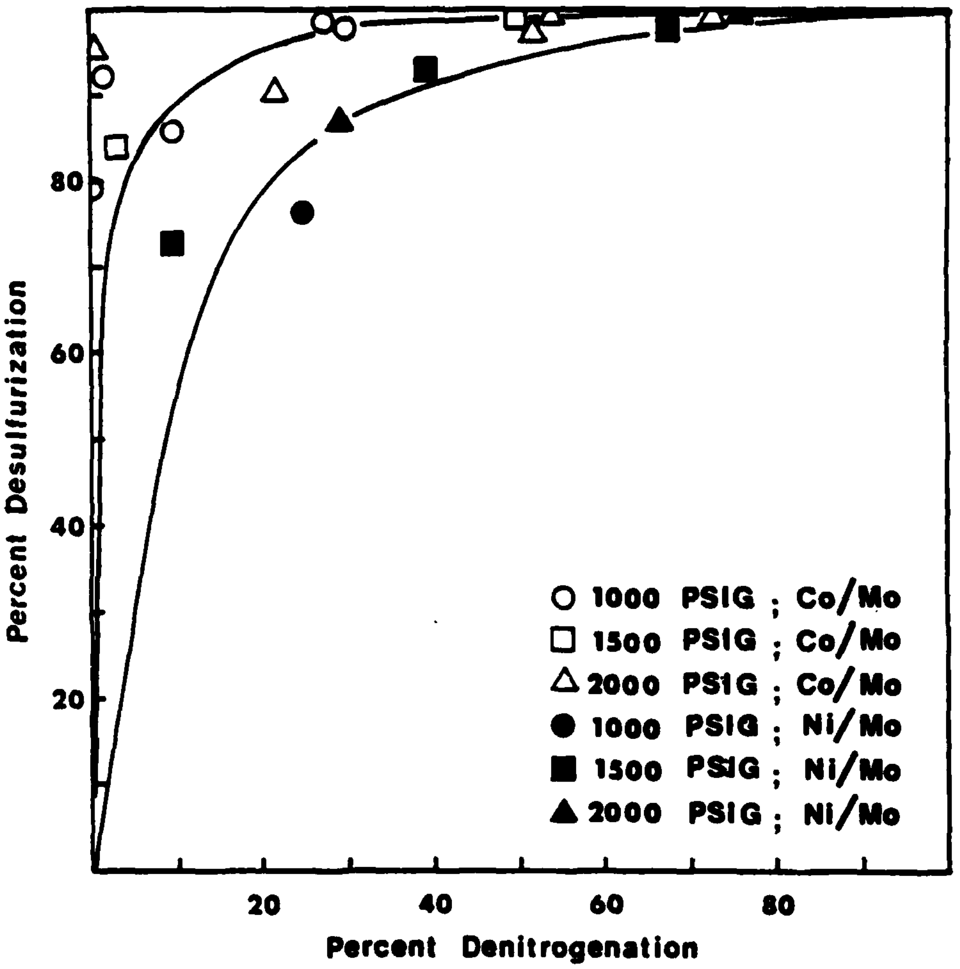


Figure IV-15. Above-ground Shale Oil Hydrotreating

Overall, there was a somewhat disappointing degree of scatter in this screening data set. Major conclusions cannot be drawn from this data, with the exception of the (expected) relative relationship between desulfurization and denitrogenation for each catalyst.

In order to better examine hydrotreater behavior, nominal 100-hour runs were performed over each catalyst. Figure IV-16 presents data for the cobalt molybdate catalyst and Figure IV-17 the nickel molybdate catalyst. From the screening data, only about two percent nitrogen removal would have been expected, but stabilized rates of 5 to 10 percent and initial rates of 20+ percent were, in fact, observed. The expected desulfurization level of 79 percent was approached, but not attained. Overall, the cobalt molybdate system demonstrated fluctuations for both sulfur and nitrogen removal as shown in Figure IV-16, with some indication that the catalyst was not completely equilibrated.

The nickel molybdate demonstrated more stability and Figure IV-17 indicates that catalyst equilibration was probably attained after about 40 hours on stream. Predicted desulfurization of 76 percent was in excellent agreement with these data, but again, the screening data and the five-day stability study data did not agree on denitrogenation levels. For this system, the screening data overstated nitrogen removal.

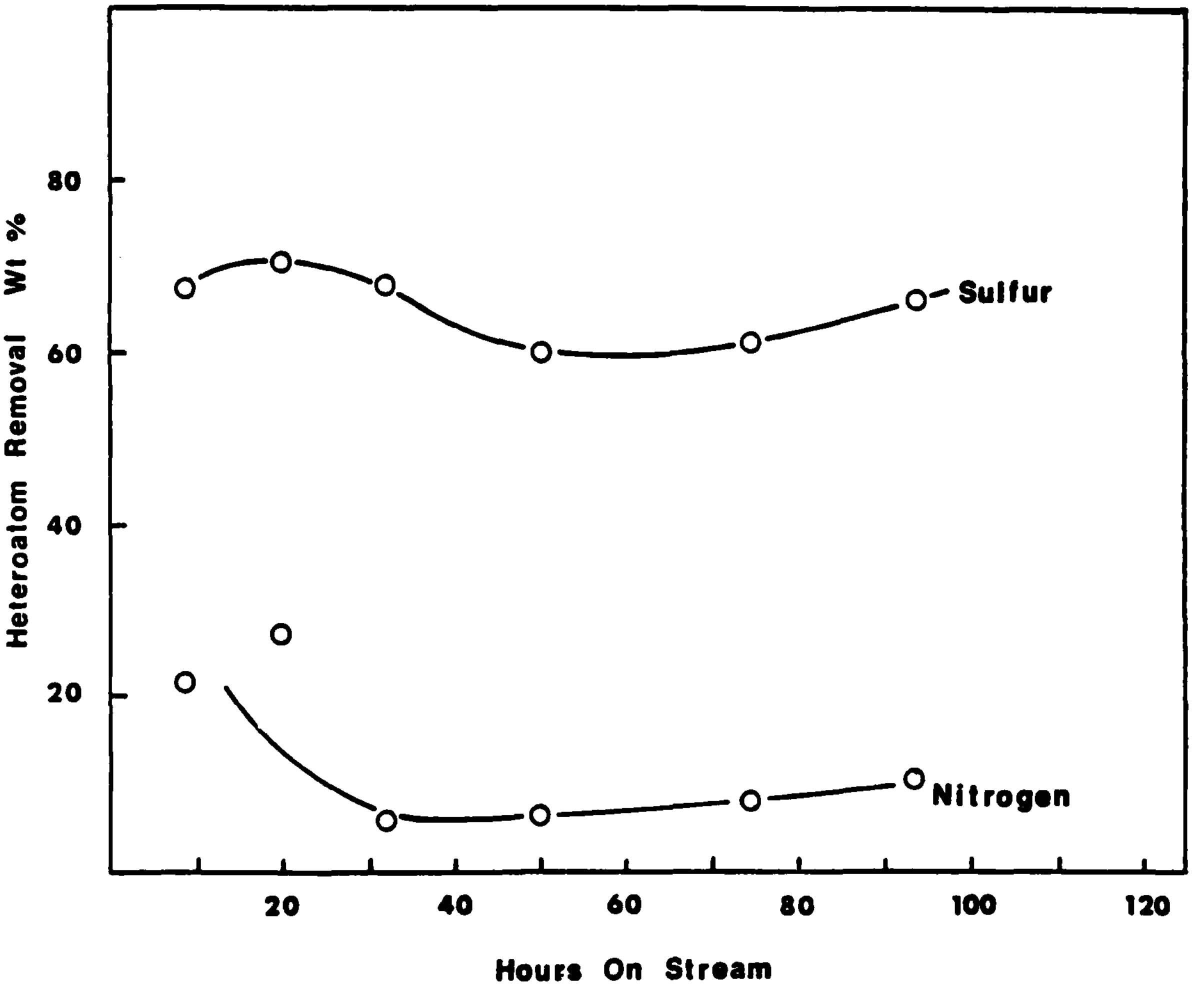


Figure IV-16. Heteroatom Removal Stability - Crude Shale Oil Hydrotreating - Series M-21

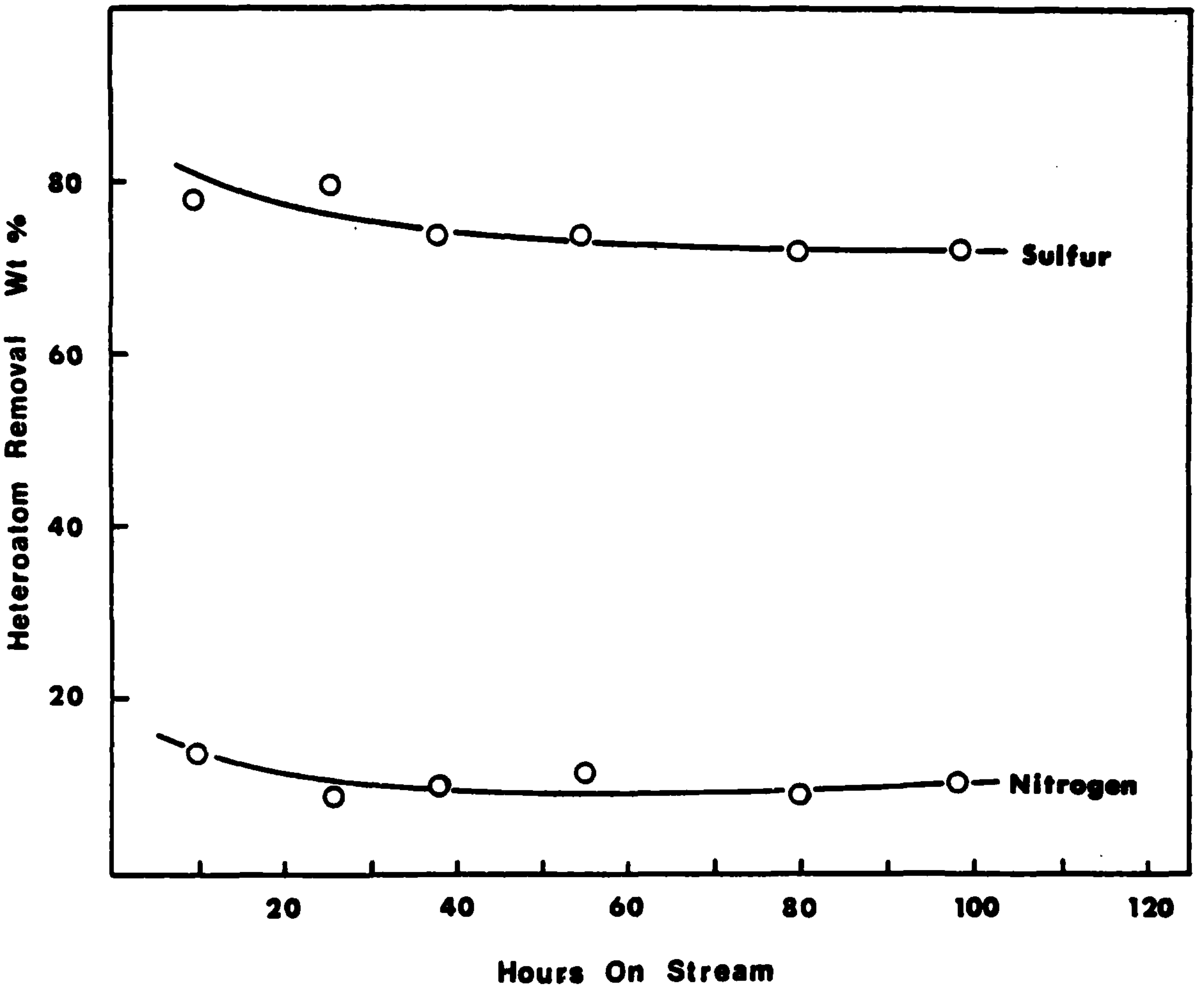


Figure IV-17. Heteroatom Removal Stability - Crude Shale Oil Hydrotreating - Series M-22

In comparison, the two catalyst systems demonstrated remarkably similar results at the end of each run. The nickel molybdate catalyst produced marginally higher desulfurization, but denitrogenation was practically identical. Actual run conditions were slightly more severe during the cobalt molybdate run, with slightly higher resulting hydrogen consumption. There are indications that more hydrogen was provided to the 600°F+ material by the cobalt molybdate system than by the nickel molybdate.

At this point, catalyst and condition selection were still indeterminate. As a result, an extended (nominal 30 days) catalyst aging run was provided for this material analogous to that performed for the in situ oil and at comparable conditions in order to provide a direct feedstock comparison. The run was reasonably stable, with the major problem encountered being pump failure. Results, as shown in Figure IV-18 and IV-19, demonstrated clear deactivation trends which had not stabilized at the end of run. Examination of the catalyst afterwards confirmed this observation.

Final analysis of these data demonstrates that slightly higher severity, probably in terms of higher pressures and lowered specific throughput, will be required for the above-ground material. Adequate maintenance of catalyst activity for commercial purposes was not attained, although observed deactivation rates were not as severe as might be expected at the pressures utilized. There are

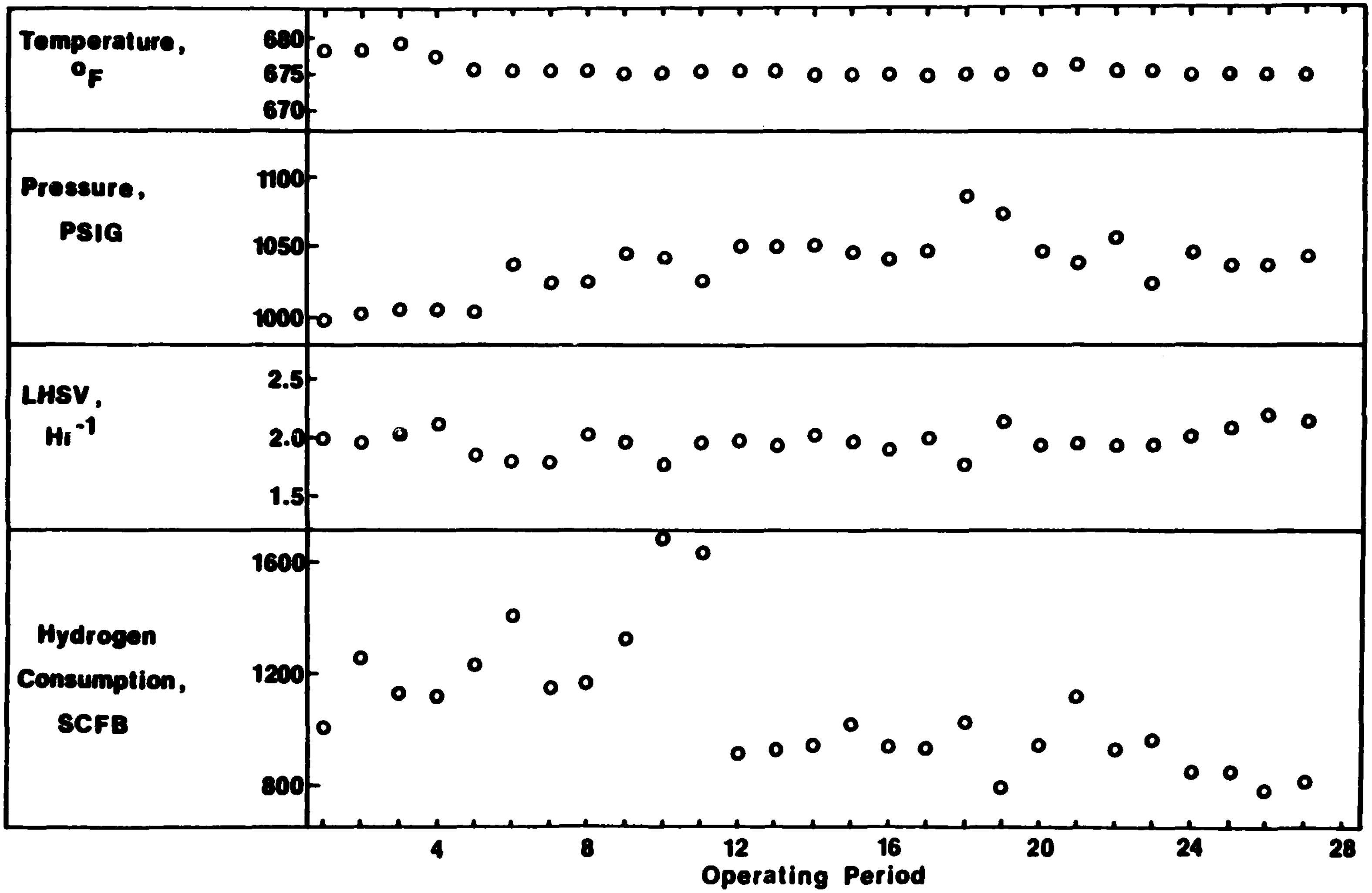


Figure IV-18. CSHT Aging Results For Above-ground Shale Oil

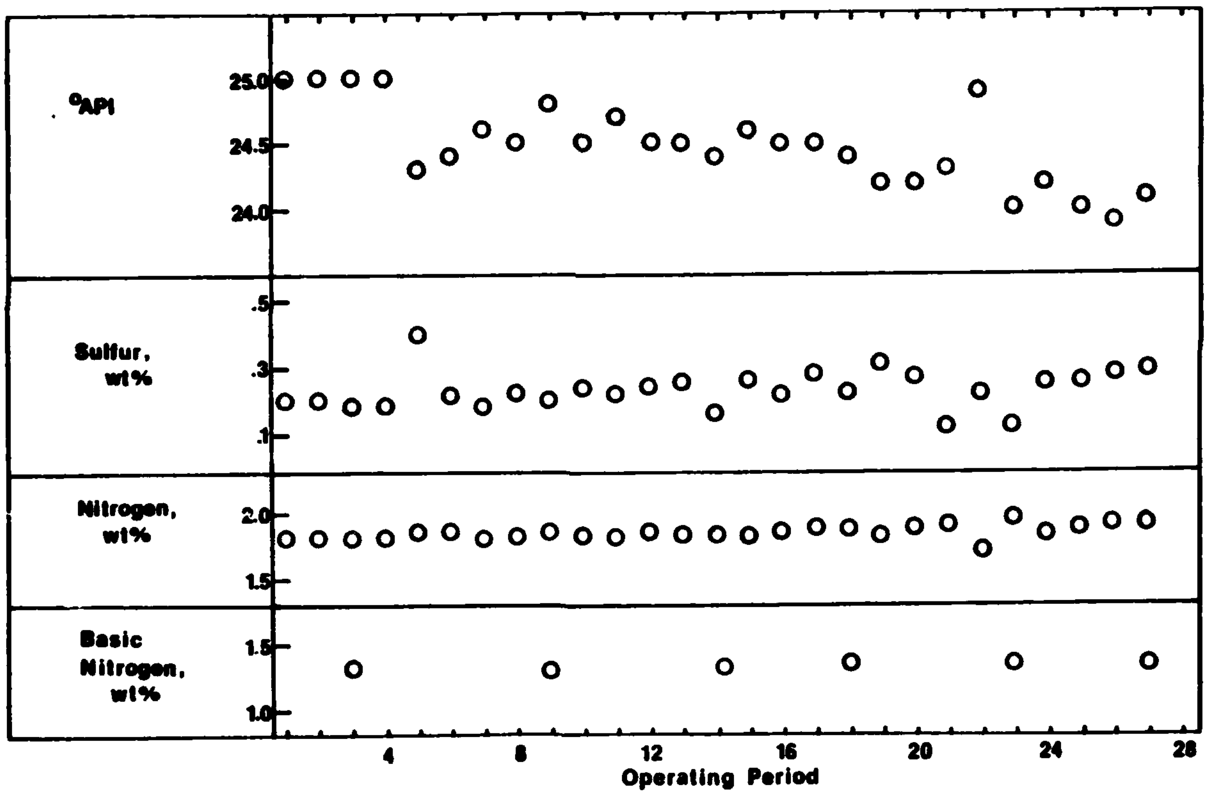


Figure IV-19. CSHT Results For Above-ground Shale Oil indications, which must be defined in detail by overall process analysis, that nickel molybdate catalyst may be preferred for this feedstock.

FEEDSTOCK COMPARISON

The most detailed available comparison of these materials is shown by the 30-day catalyst stability studies. These runs, performed over cobalt molybdate catalyst at comparable conditions, provide a comparison of both product properties and aging trends at those conditions. Figure IV-20 compares product API and sulfur values, plus (stabilized) hydrogen consumption (linearized, based on days 12 to 30). As can readily be seen at these conditions, the in situ product is superior, showing lower catalyst activity decay rates, at lower hydrogen consumption.

Figure IV-21 presents a comparison of product nitrogen trends. Again, the in situ material shows lower decay rates and superior product properties.

As a point of further interest, Figures IV-22 and IV-23 present start-of-run desulfurization and denitrogenation trends at comparable conditions for these feedstocks. Since these materials would, in fact, be competitors with petroleum, response curves from other studies for petroleum vacuum gas oil are also shown for comparison. The petroleum oil represents what has earlier been defined as a conventional feedstock, with roughly 1.2 weight percent sulfur and about 400 ppm total nitrogen. Of particular interest,

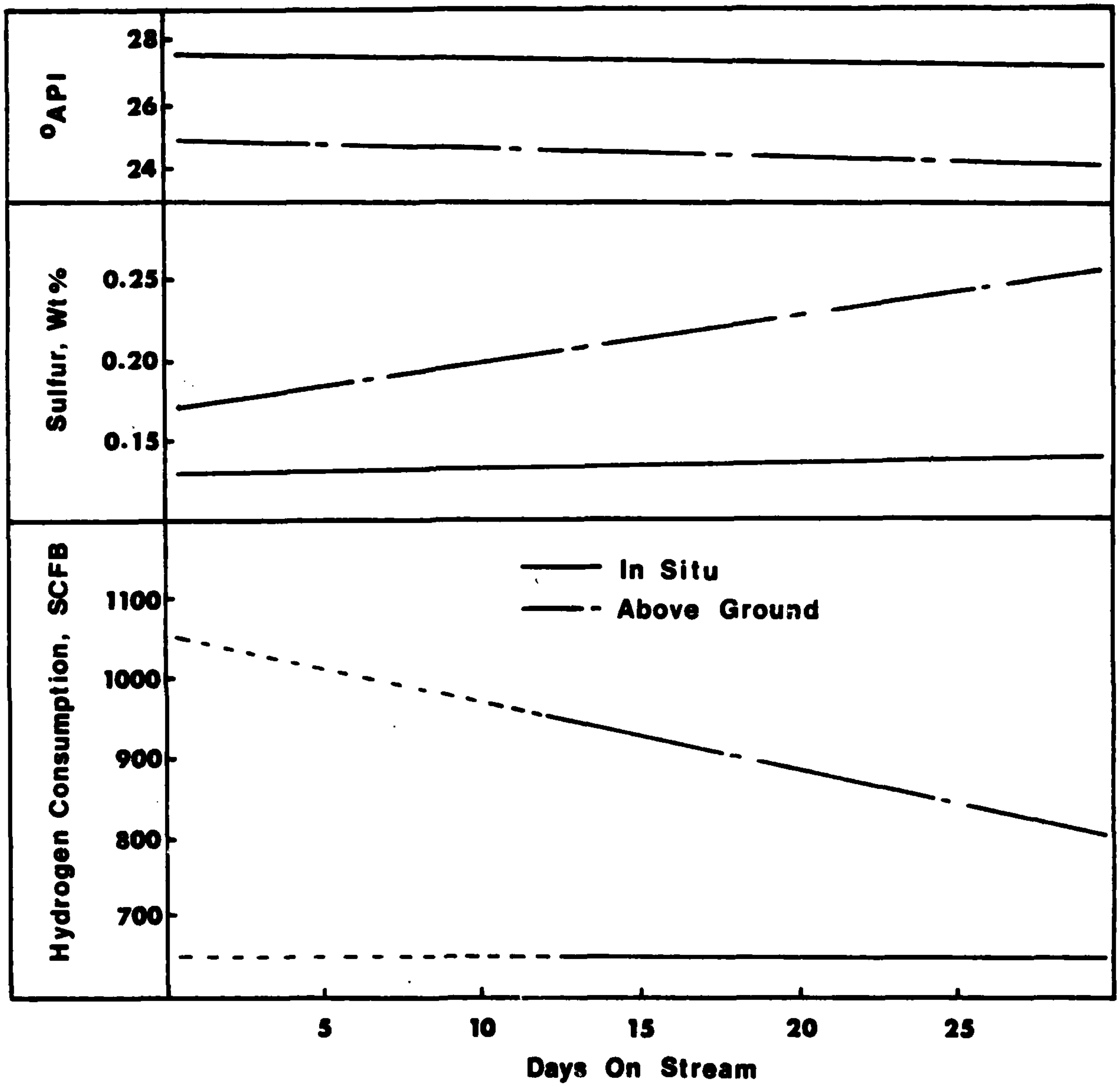


Figure IV-20. Comparison Of Hydrotreater Aging Results For Each Oil

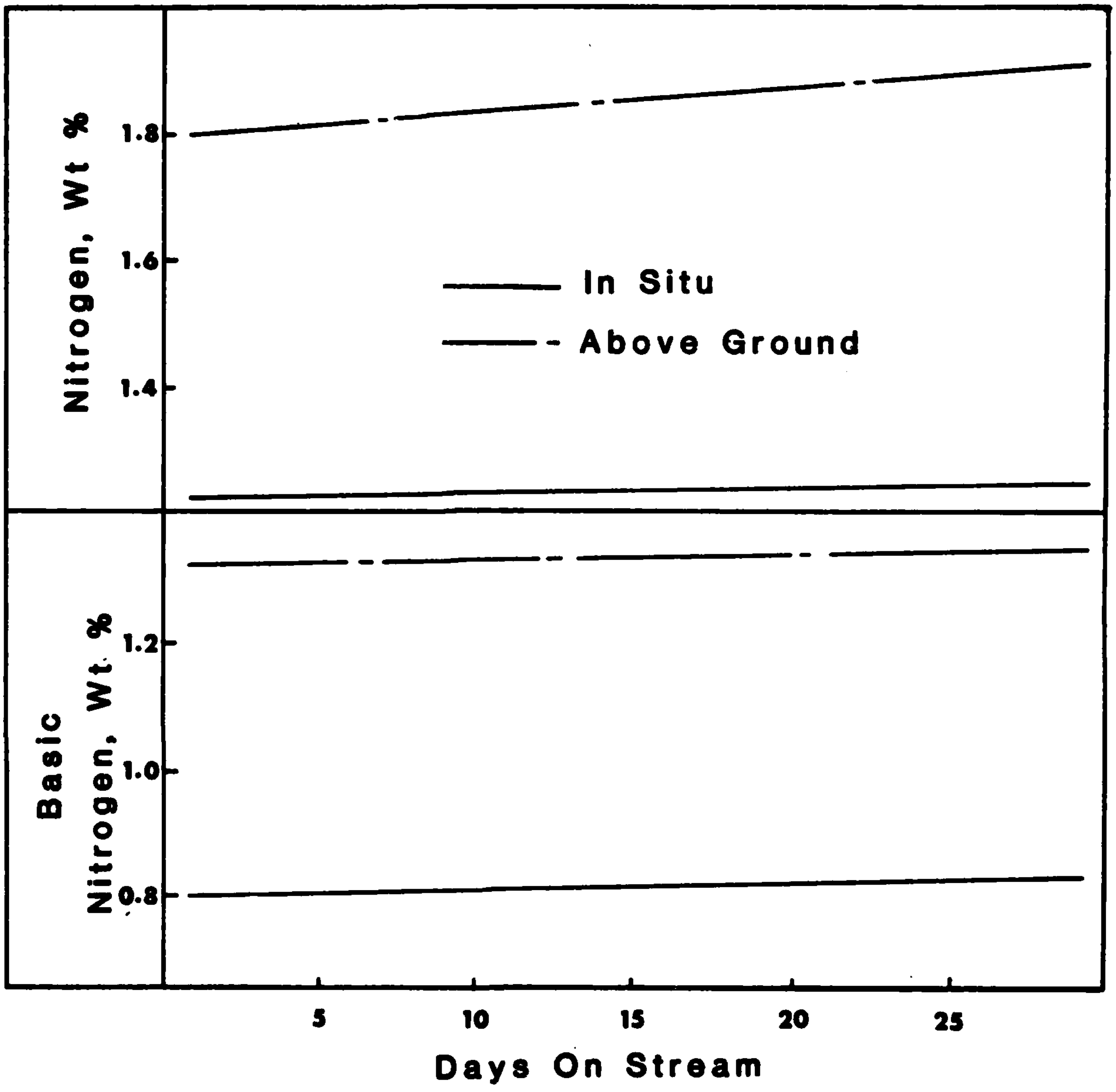


Figure IV-21. Comparison Of Hydrotreater Aging Results For Each Oil

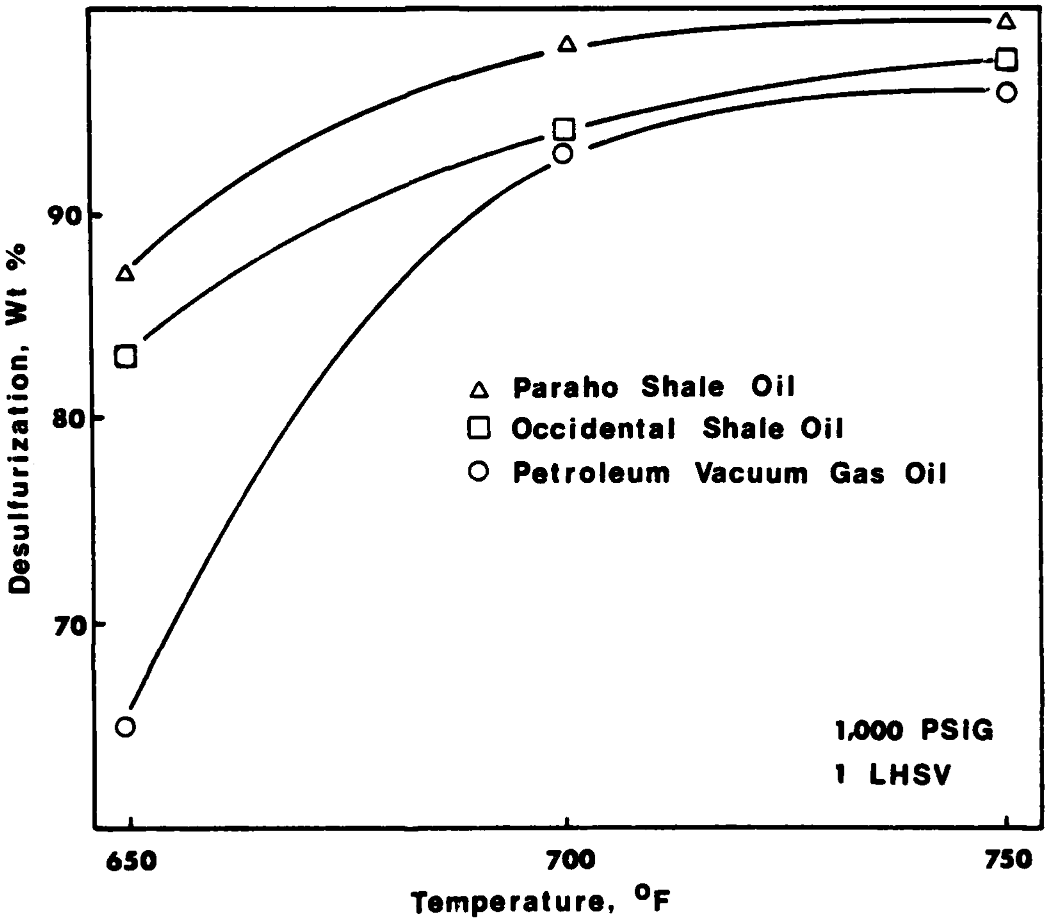


Figure IV-22. Desulfurization Comparison For Shale Oil And Petroleum

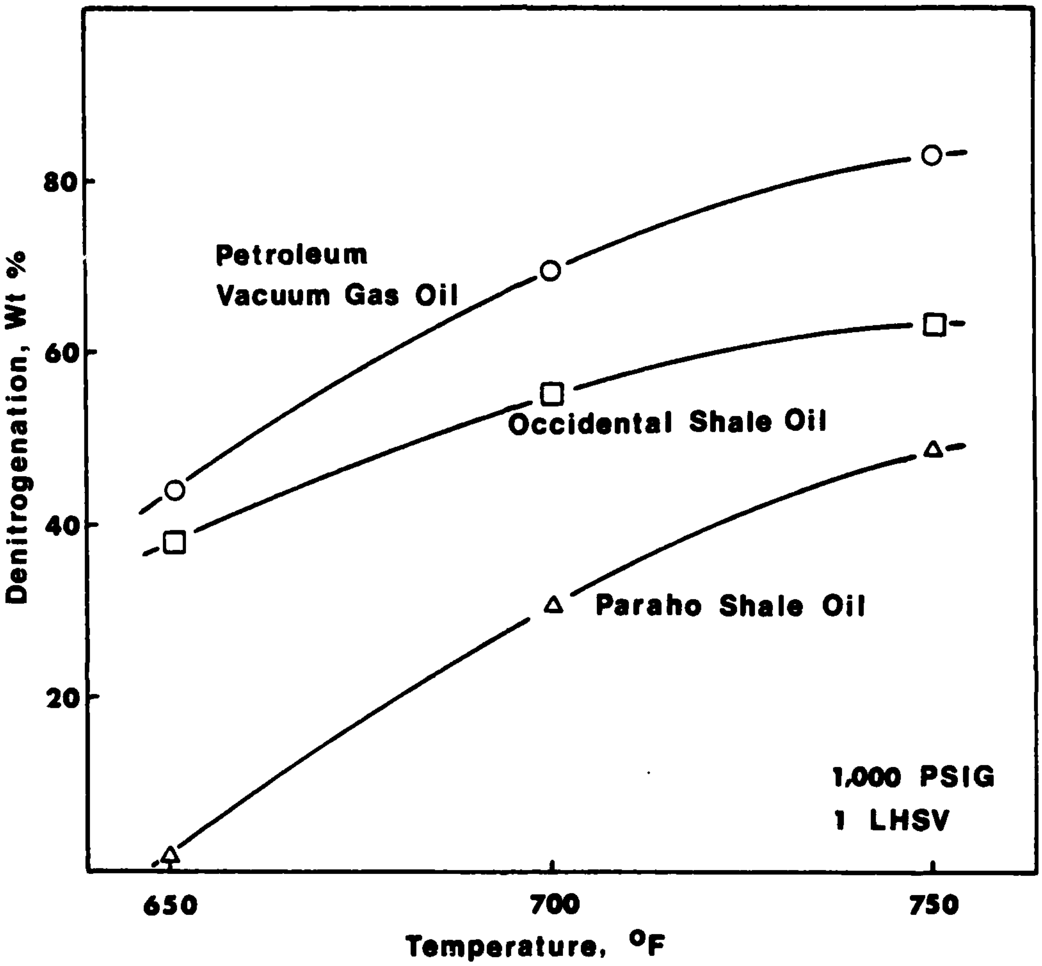


Figure IV-23. Denitrogenation Comparison For Shale Oil And Petroleum the shale oils demonstrate higher desulfurization, but lower denitrogenation rates than the petroleum oil. In both cases, the above-ground shale oil presents extremes - highest desulfurization, but lowest denitrogenation. The in situ oil is intermediate for both cases. Data are not readily available for the previously defined incremental petroleum feedstocks, but one would expect each of these curves to tend to converge for that material.

In summary, the in situ oil is more amenable to hydrotreatment than the above-ground material at these conditions, and more closely approaches conventional petroleum response than the above-ground oil. The cost of processing the in situ oil will probably be lower than the above-ground oil, primarily due to the lower hydrogen consumption and to the higher pressure probably required for the above-ground material.

3. Fluid Catalytic Cracking. An extensive data set for fluid catalytic cracking of both in situ and above-ground oils was developed. Major alternatives of feedstock quality and operating severity were evaluated.

IN SITU

Major data sets for in situ oil were developed comparing: (1) hydrotreater severity, (2) hydrotreater catalyst type and (3) recycle crackability. Further studies were also performed to evaluate the impact of blending nitrogen extract to the FCC charge and using a full range feedstock for selected materials. Detailed product properties were developed. Table IV-3 keynotes the FCC module.

Figure IV-24 portrays major functionalities of the FCC operation correlated with basic nitrogen content of the feedstock. The conversion level (based on 600°F) at which the maximum C_5 to 600°F yield is obtained decreases rapidly with increasing feedstock basic nitrogen content. However, the maximum C_5 to 600°F yield, while declining initially, appears to stabilize at about 1.0 weight percent basic nitrogen. Of particular interest, this stabilization of maximum C_5 to 600°F yield occurs even though the C_5 to 400°F yield continues to decline sharply. This implies a transition in selectivity as basic nitrogen content increases towards production of distillate products (400 to 600°F), rather than naphtha or gasoline (IBP to 400°F).

Figure IV-25 expands the maximum C_5 to 600°F yield curve over a range of conversions. The envelope developed shows the relationship between the three levels of basic nitrogen content. Of major interest, there appears to be very little difference in yield between these materials at low (<50%) conversion. EXTRACTACRACKING utilizes this phenomenon by operating at relatively low conversion, with high basic nitrogen content feedstock, while utilizing high recycle rates to obtain the required total conversion.

Yields are further subdivided into naphtha (I to 400°F) and distillate (400 to 600°F) fractions in Figure

TABLE IV-3

FLUID CATALYTIC CRACKING

Objectives: Convert an economic maximum of +600°F material into turbine fuel and gasoline boiling ranges. Provide concurrent heteroatom removal and hydrogen redistribution.

Key Element: Economic maximum distillate production

Parameters Evaluated:

- Operating severity
- Hydrotreater source parameters
- Shale oil type

Unique Features:

- High nitrogen feedstocks
- Production emphasis on distillate plus gasoline ranges

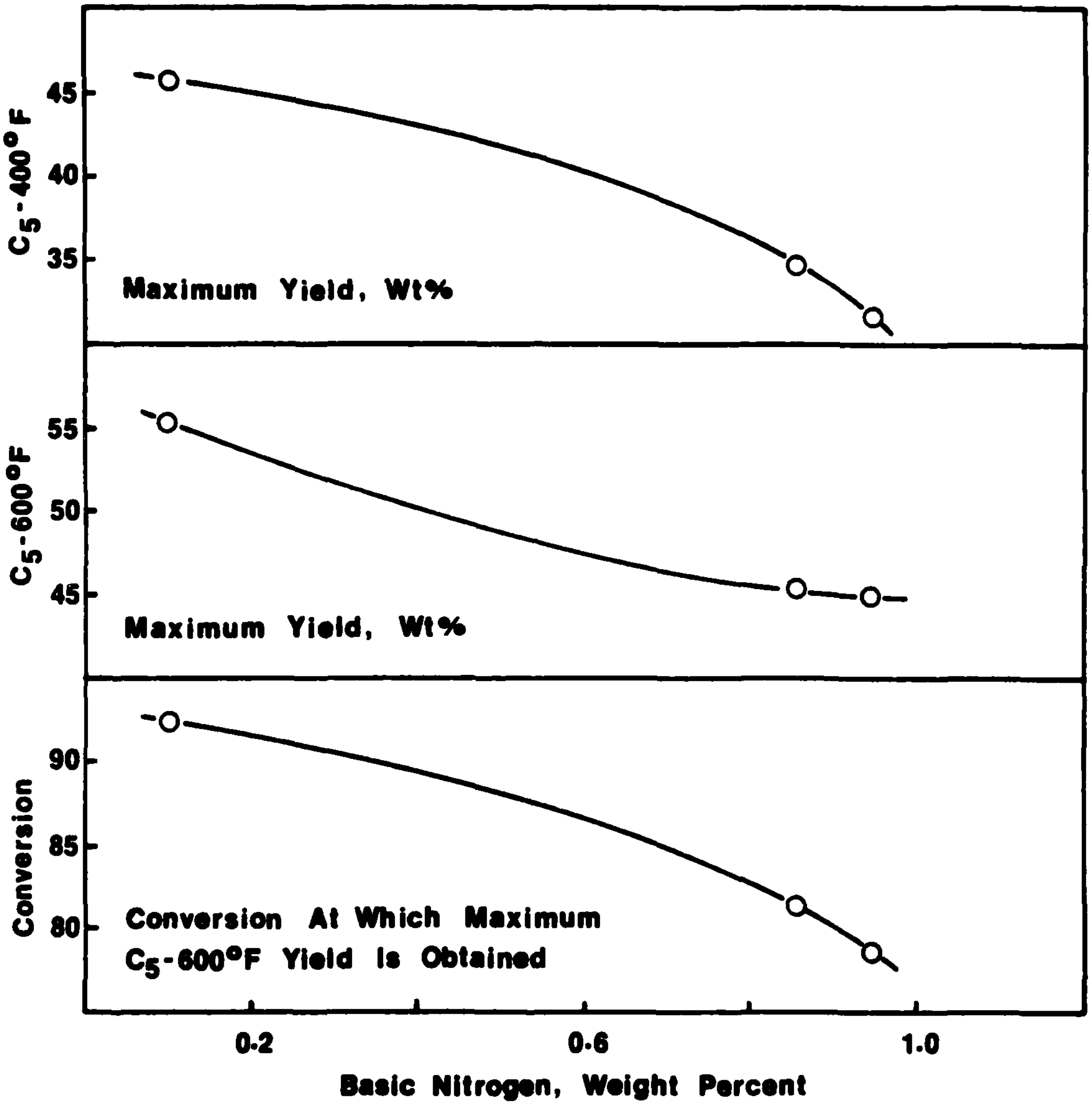


Figure IV–24. FCC Yield Maxima Dependence On Feedstock Basic Nitrogen Content For In Situ Shale Oil

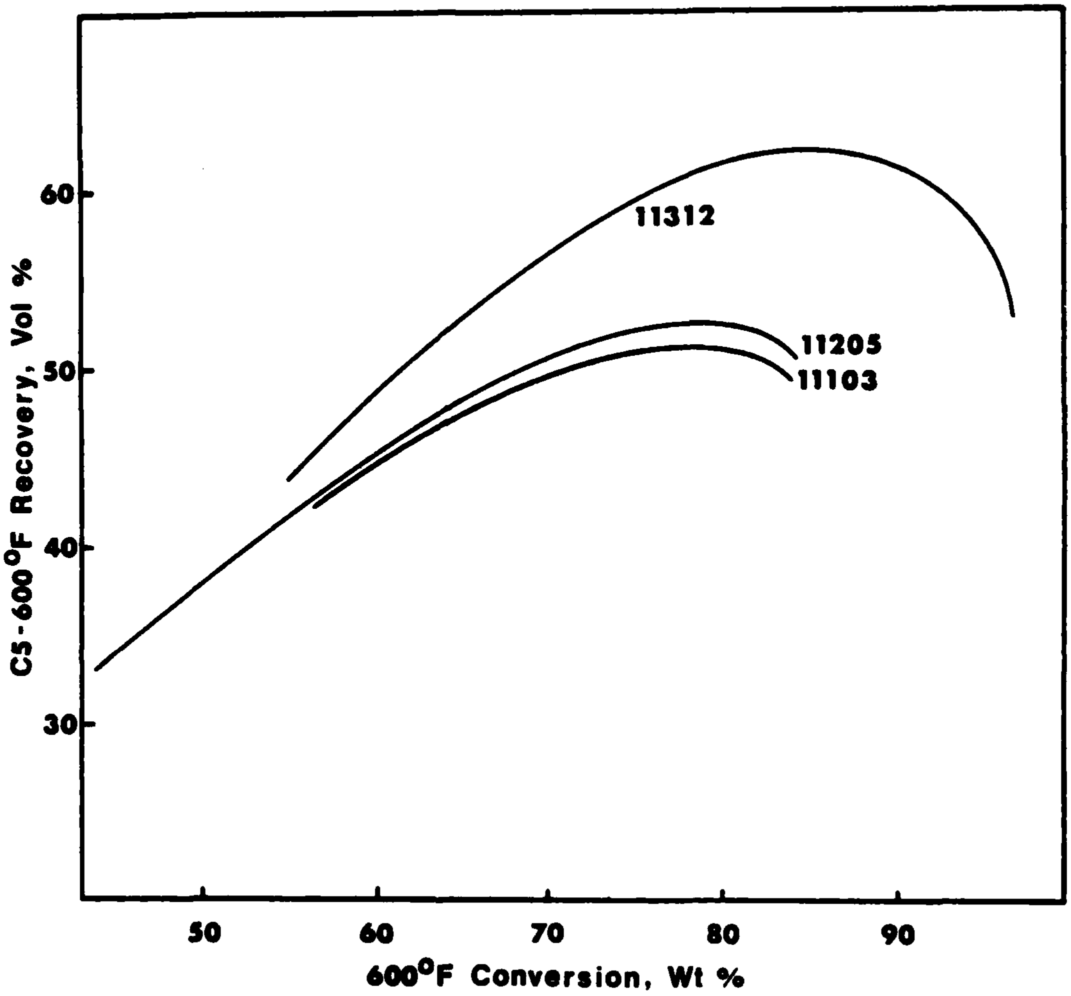


Figure IV–25. FCC Combined Distillate Yields As A Function Of Hydrotreater Severity

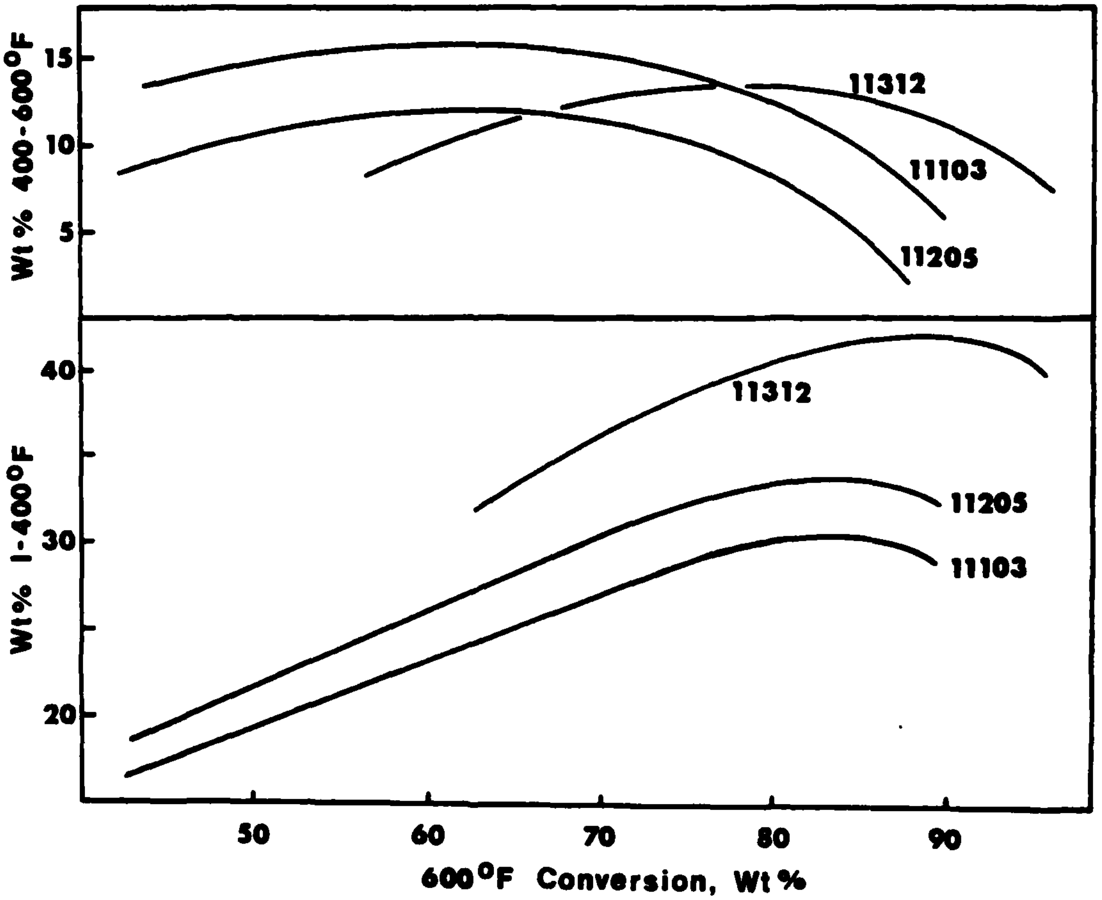


Figure IV-26. FCC Naphtha And Distillate Yields As A Function Of Hydrotreater Severity

IV-26. The naphtha yields clearly show the effect of basic nitrogen, with naphtha yield suppression at the higher feedstock levels. The distillate yields, however, are somewhat confused due to high yields at high conversion in the severely hydrotreated sample. Below about 60 percent conversion, however, the trend of higher distillate yields with higher basic nitrogen content appears.

Gas and coke trends are shown in Figure IV-27. As expected, the lower basic nitrogen content feedstock produces lower coke. However, the magnitude of difference is small, which is somewhat surprising. Gas yields are essentially identical, being more a function of severity than basic nitrogen content. However, there is a very slight indication that the lower basic nitrogen content feedstocks may make more gas, which is again surprising.

The basic nitrogen content functionalities described above were based on cobalt molybdate hydrotreated stocks. Most commercial FCC feed hydrotreaters utilize nickel molybdate catalyst, so a nickel molybdate hydrotreated sample was also processed. Figures IV-28 and IV-29 compare results for two samples hydrotreated over the different catalysts, but at comparable conditions. Naphtha and total IBP to 600°F yields are very similar, but the nickel molybdate sample produced higher distillate (400 to 600°F) yields at comparable or lower gas and coke production. In all cases, however, except for distillate and coke yields at high conversion, the differences were relatively small. Sample

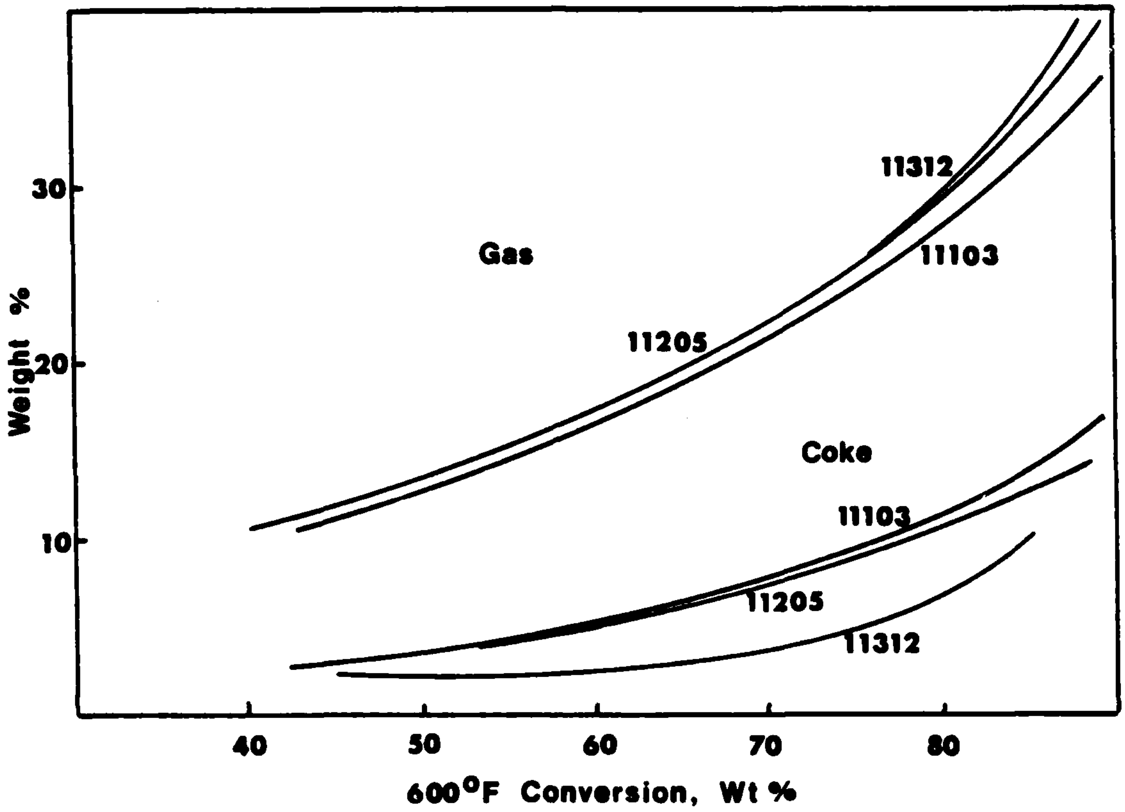


Figure IV-27. FCC Coke And Gas Yields As A Function Of Hydrotreater Severity

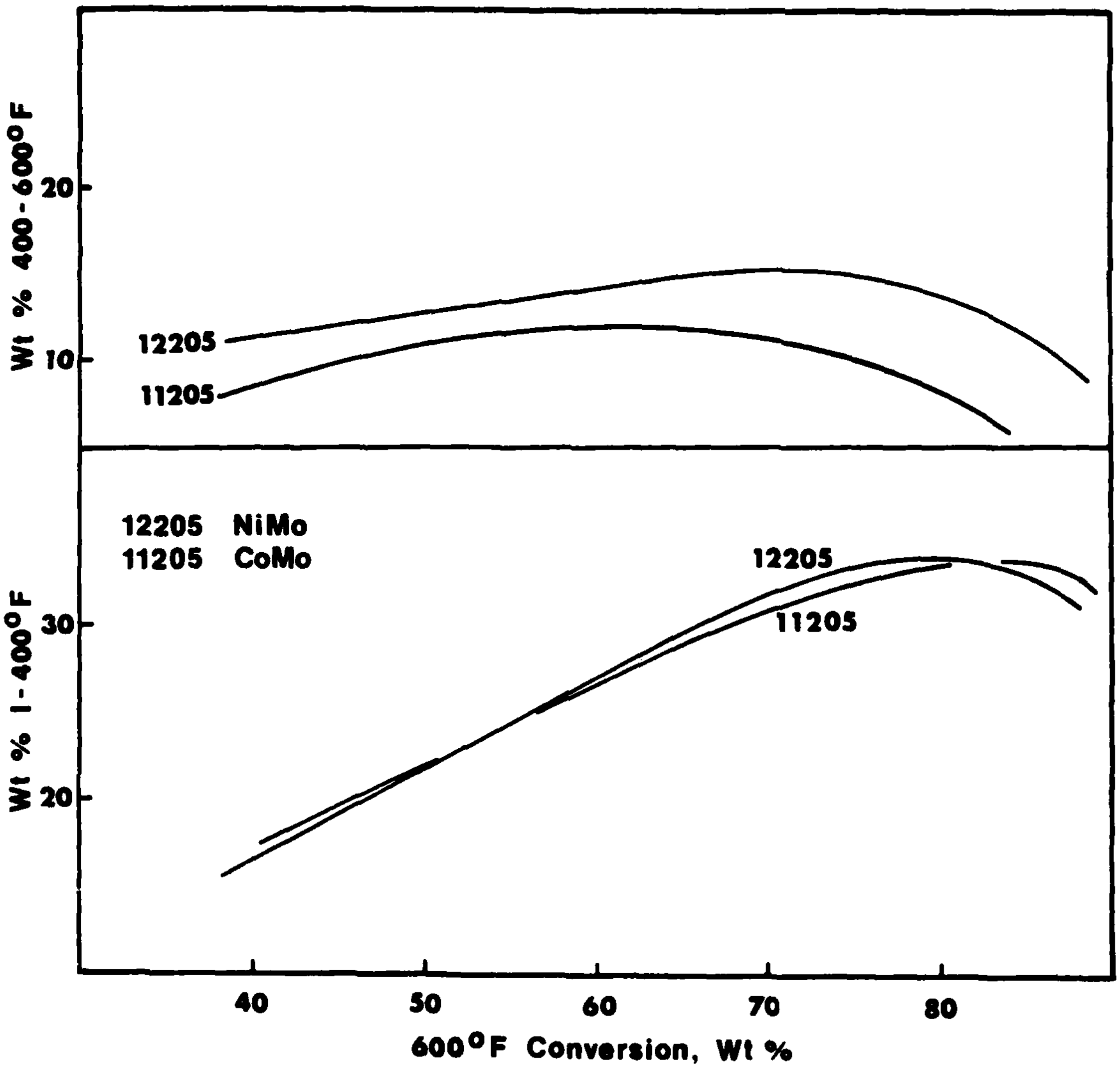


Figure IV-28. Comparison Of FCC Naphtha And Distillate Yields For Nickel And Cobalt Based Hydrotreating Catalysts

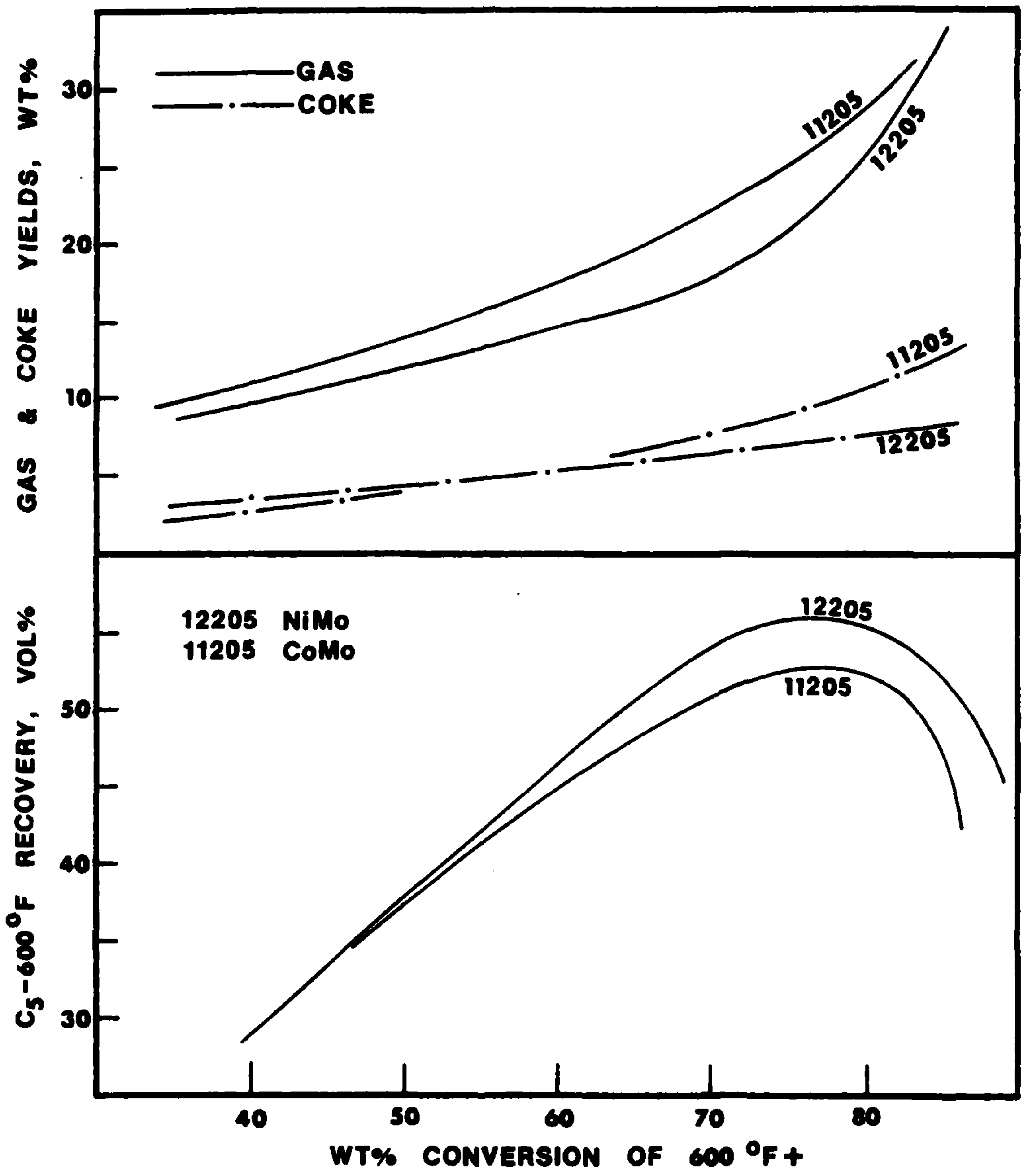


Figure IV-29. FCC Coke, Gas And C_5-600°F Yields As A Function Of Hydrotreater Catalyst production data during hydrotreating indicated a much lower hydrogen consumption for the cobalt molybdate sample. Based on these factors, and the trend probability that FCC fresh feed operations would be in the range of 40 to 60 percent conversion where there were only slight differences in FCC response, there is high probability that the cobalt molybdate system would be the desired choice for preparation of FCC feedstock.

One further fresh feedstock analysis was also performed. There are distinct problems at present in disposing of the nitrogen extract produced in the extraction module. One possible point of disposal, if in fact the FCC unit can provide a denitrogenation function, is to blend this extract to FCC feed. Results from this analysis are shown in Figures IV-30 and IV-31 where the doped sample actually showed higher distillate and comparable naphtha yields than a corresponding original fresh feed sample. The total C_5 to 600°F recovery is also apparently enhanced, and gas and coke yields reduced, by addition of the extract. These results are startling, and, while they must be confirmed by Phase III work, utilization of the extract in this manner could be of tremendous importance to the process.

The final crackability, or MAT, study performed was for an FCC bottoms (600°F+) material which had been hydrotreated for recycle. As shown in Figures IV-32 and IV-33, crackability of these materials is increased dramatically

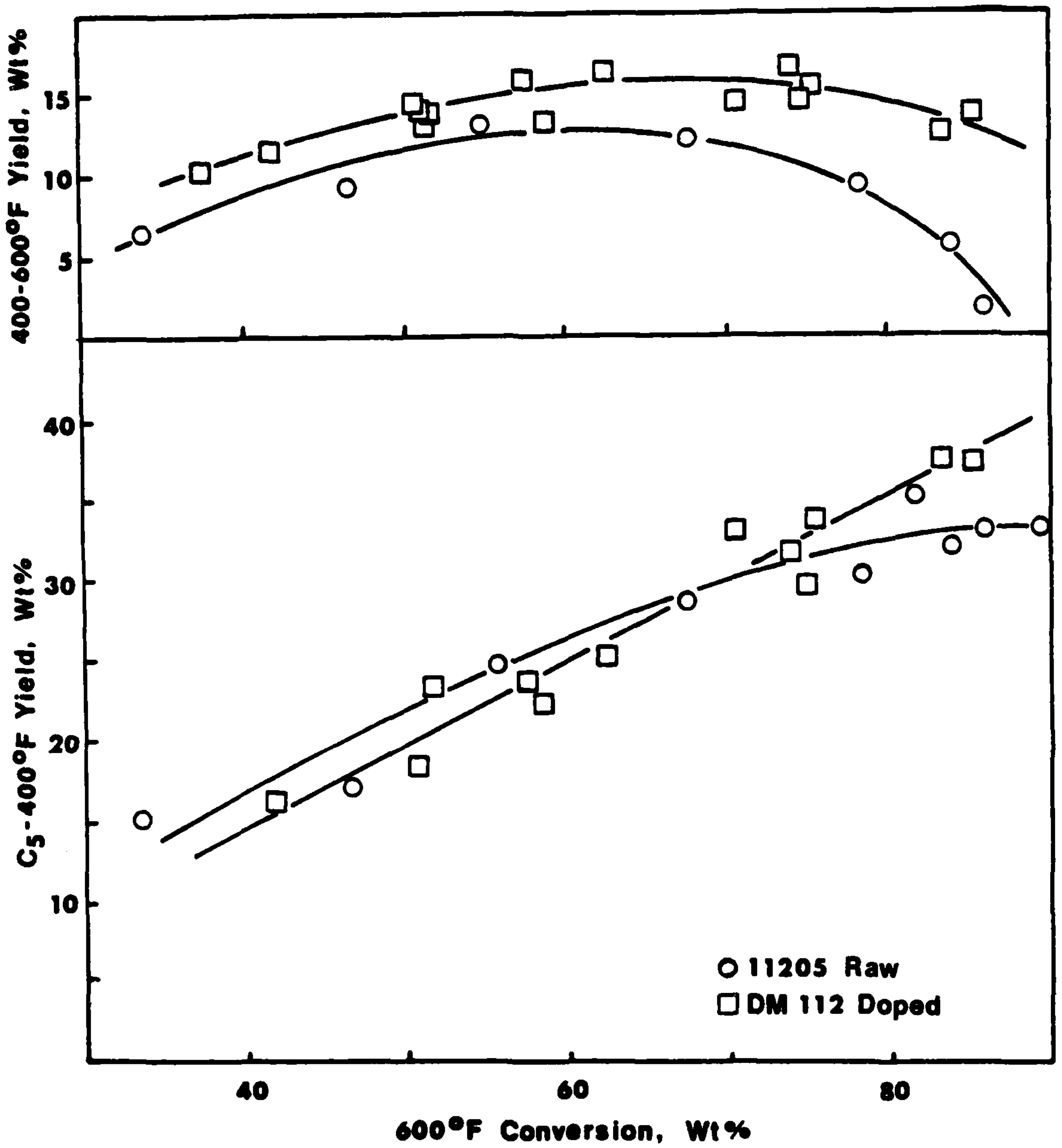


Figure IV-30. Comparison Of Nitrogen Doped And The Analogous Fresh Feed Yields

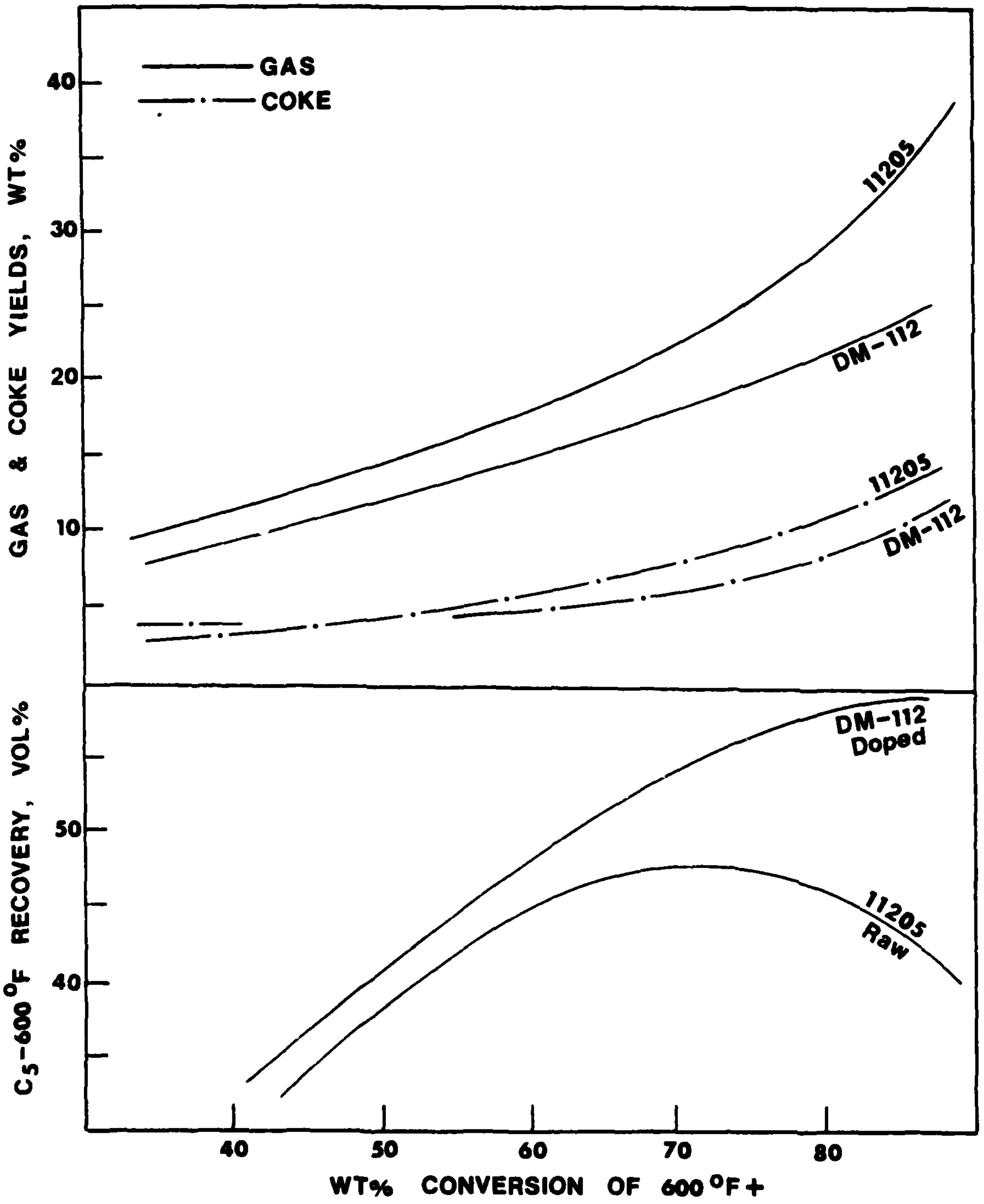


Figure IV-31. Comparison Of Crackability For A Nitrogen Doped Feed And An Analogous Fresh Feed

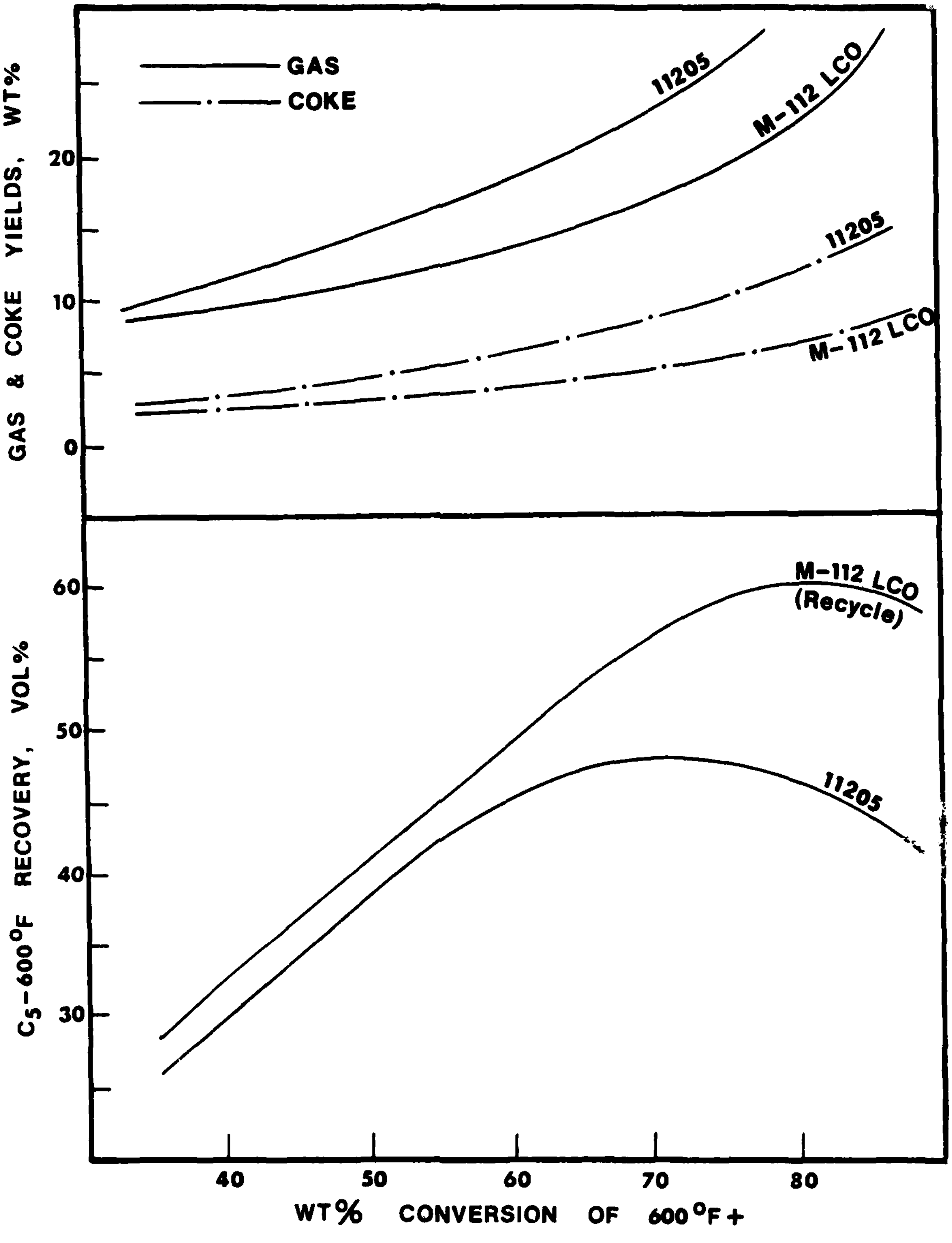


Figure IV-32. Effectiveness Of Sending A Hydrotreated Recycle Stream To The FCC

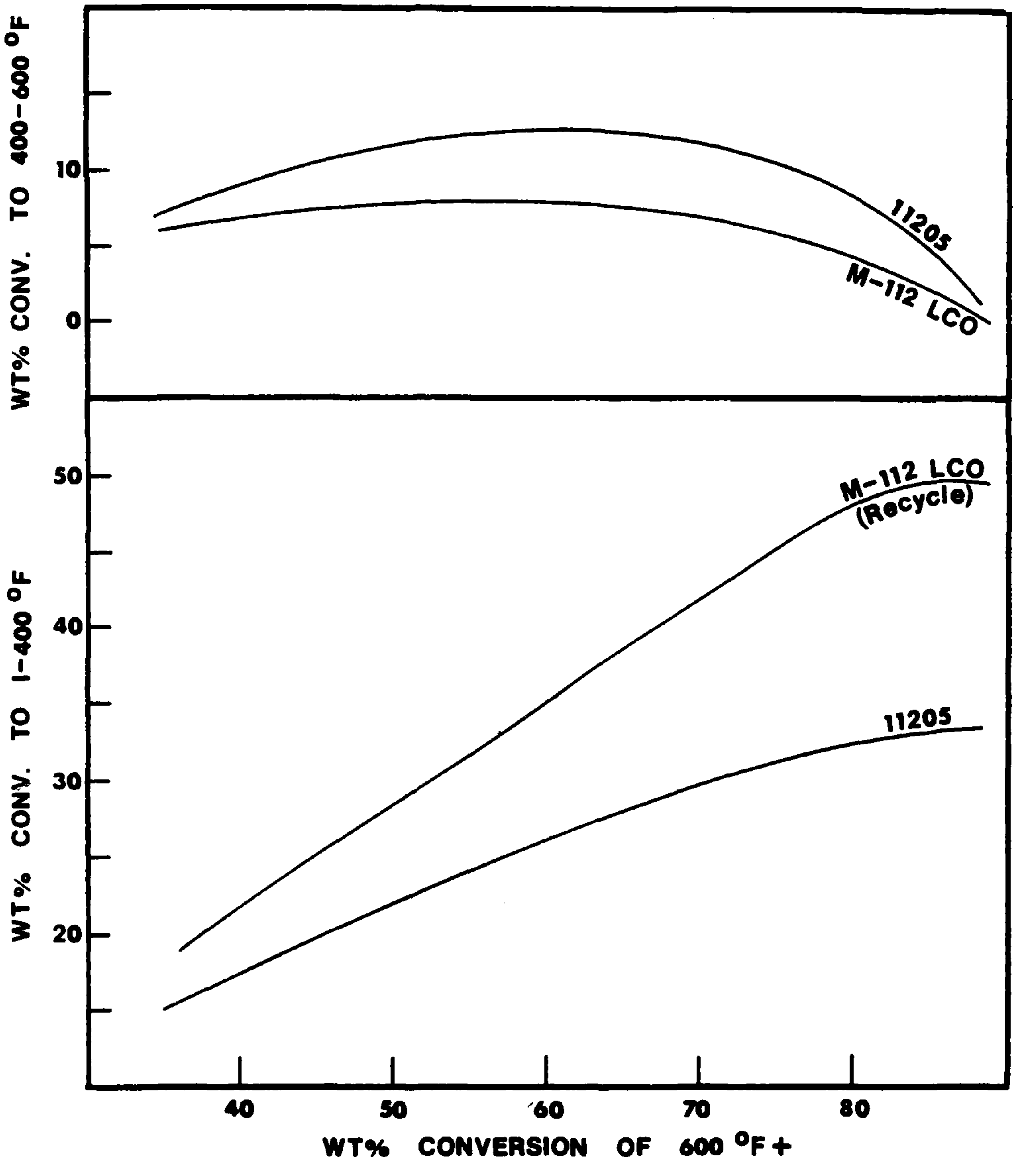


Figure IV-33. Comparison Of Naphtha And Distillate Yields For The Cracking Of A Hydrotreated Recycle And A An Analogous Fresh Feed compared to the original fresh feedstock. In particular, the selectivity to naphtha is increased by the greatest amount. These data confirm original projections of both recycle capability and the improved character of the recycle material.

In order to prepare samples for further processing, obtain larger scale data, and obtain product quality data, tests were also performed on a continuous circulating unit (FCR). Feedstocks were two samples, prepared under analogous conditions, with the exception of hydrotreater catalyst - one cobalt molybdate based and one nickel molybdate based. Results are shown by the triangular data points overplotted on MAT data in Figures IV-34 and IV-35, respectively. The graphs are consistent in that both gas and C_5 to 600°F yields are lower, and coke higher, than the MAT data. These discrepancies are almost certainly due to mechanical limitations in the stripping section of the circulating unit. Temperature and residence time factors in that unit result in less efficient stripping than in either the MAT or commercial units. As partial proof, consider the cobalt molybdate data in Figure IV-34. If, in fact, the coke yield is overstated on the FCR by the differential of 7 percent between the MAT curve and FCR data point, and if this material is unstripped 600°F+ material ("catalyst coke"), then the true conversion would be about 50 percent. Volumetric yields would then be in substantial agreement with the MAT data, while gas yields would still

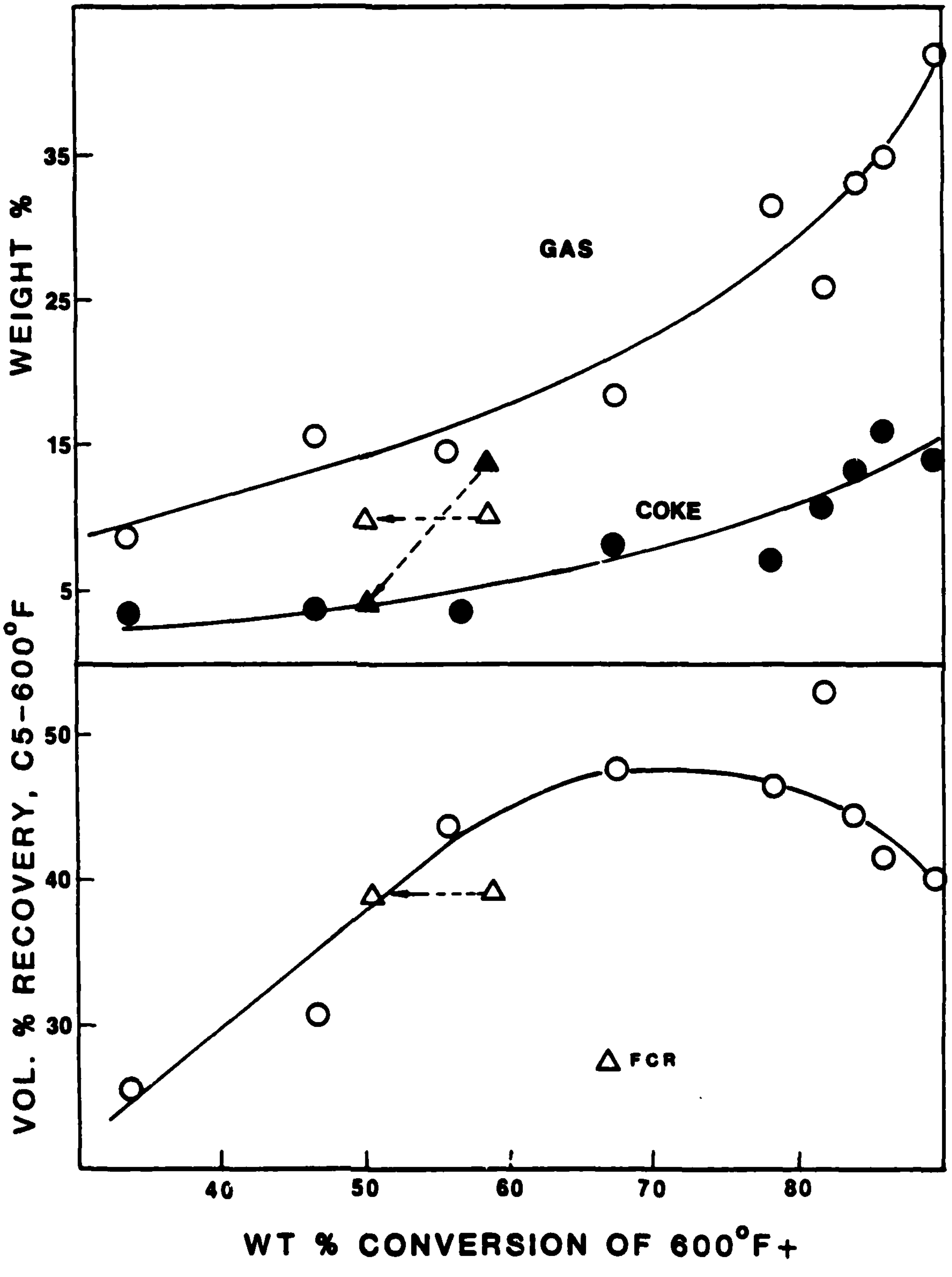


Figure IV-34. Comparison Of FCR And MAT Results

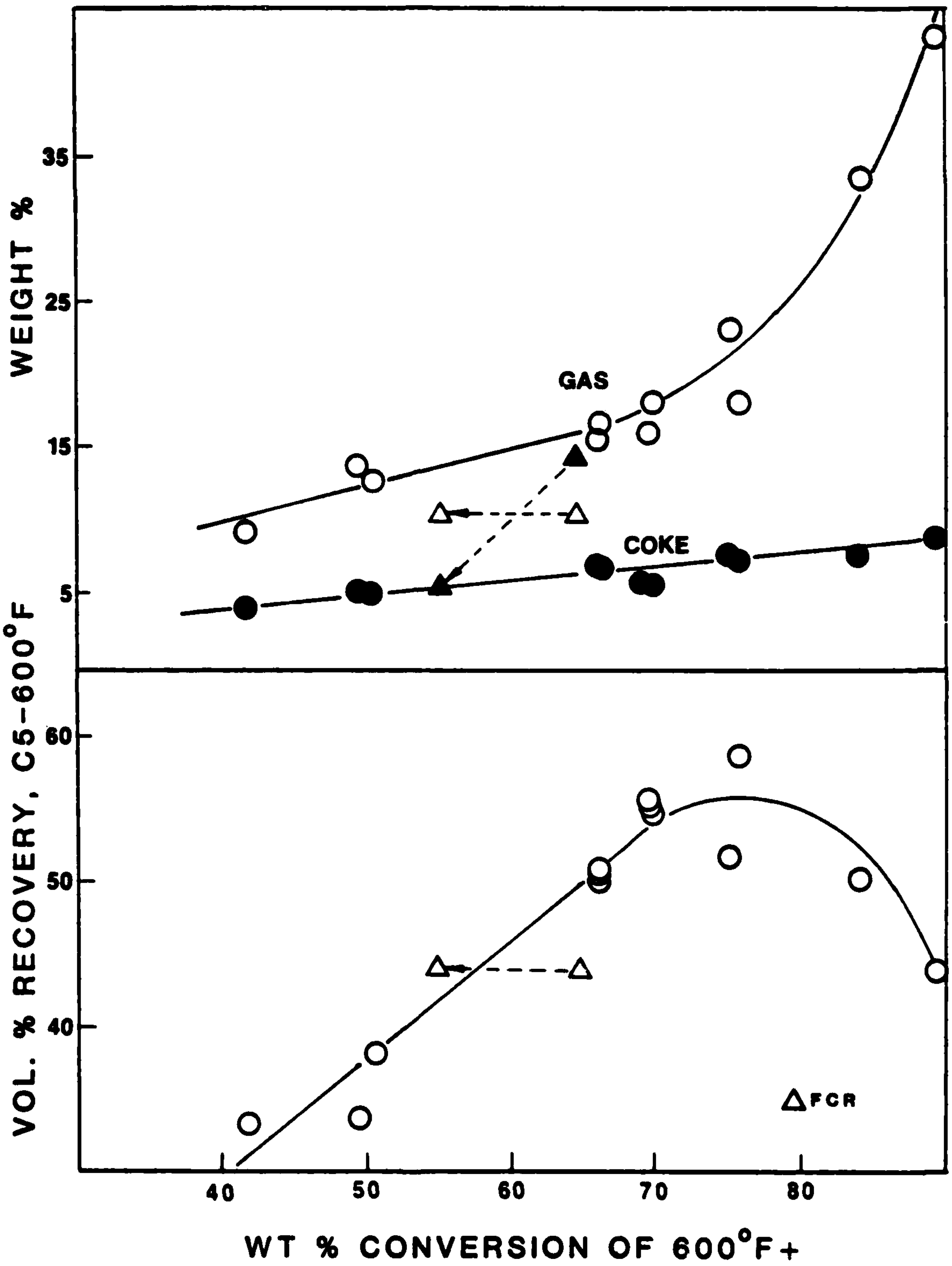


Figure IV-35. Comparison Of FCR And MAT Results be slightly low. There is always the possibility, of course, that the MAT data understate coke and overstate gas yields. In particular, since conversion was attained by exceedingly high catalyst-to-oil ratios in the FCR, and by temperature (for the most part) in the MAT tests, the possibility occurs that slightly higher coke (due to catalyst coke factors) and lower gas (due to lower temperature at equivalent conversion) are real, at least on a corrected basis. All three factors are probably present. With the correction, however, and the further caution above, the data are in substantive agreement for both feedstocks.

The final FCR run processed the hydrotreater aging product. The feedstock also differed in that full range, rather than fractionated, product was used as charge. These runs demonstrated that full-range feedstocks result in marked reduction of distillate yields while increasing coke and gas. On a corrected basis, distillate yield ranged from only about 12 volume percent to about 22 volume percent of feed. Coke and gas yields were similarly impacted and showed a marked increase. On this basis, therefore, use of full range chargestock to the FCC unit was deleted from further consideration.

Further interest in these materials was concerned with product properties. Marked improvement in nitrogen content was obvious with roughly 25 percent denitrogenation shown by comparing total liquid product to the feedstock for the +600°F chargestocks. The full-range chargestocks showed equivalent or greater nitrogen removal, as well as 50 percent or better basic nitrogen removal. In five of the six samples processed, desulfurization was also shown. However, desulfurization results seemed to show a consistent sulfur level in the products, irrespective of feedstock sulfur level or boiling range. This could be the result of no real desulfurization, with only recombinant sulfur (due to oxidation prior to stripping after hydrotreating) removed by the FCC unit. Removal of oxygen in the cracker is indeterminate due to a sparsity of data.

Finally, excellent hydrogen partitioning was demonstrated by these materials. For feedstocks with hydrogen contents ranging from an estimated 11.3 to 12.0 weight percent distillate and residual products showed hydrogen contents from 11.8 to 13.0 and 11.6 to 11.9, respectively.

These data result in selection of fractionated product for cracking, with the cracker operated in the 50 to 60 weight percent conversion range with high recycle rates to prevent excessive coke and gas production. Based only on these data, nickel molybdate hydrotreater catalyst would probably be selected. However, the accrued hydrogen consumption owing to use of the nickel molybdate catalyst leads to the conclusion that until true optimization can be performed, the cobalt molybdate catalyst should be used. Further, due to the character of the hydrotreater recycle stream, the fresh feed and recycle should not be admixed but should be processed through separate FCC units. The fresh feed cracker would operate at moderate (50 to 60 percent) conversion, while the recycle cracker would operate at high (70 to 80 percent) conversion to take advantage of naturally lowered coke and gas yields, sharply increasing (with conversion) recoveries and improved selectivity to naphtha. If the yields for extract-extended, fresh feedstock can be confirmed in Phase III, extract blending to the fresh feed cracker should also be practiced.

ABOVE-GROUND

Data sets were developed for the above-ground oil in a manner similar to the in situ material. Data comparing the effectiveness of an FCC on feeds produced by the hydrotreater operating at different severities with cobalt molybdate catalyst are shown in Figures IV-36 and IV-37. Like the in situ, the higher severity hydrotreated (lower basic nitrogen) material produced lower coke and better naphtha yields. However, somewhat surprisingly, the high severity sample produced more gas, lower distillate and lower total C_5 to 600°F yield. The reason for this depressed yield is not readily apparent.

The hydrotreater catalyst comparison, Figures IV-38 and IV-39, shows only small differences. The cobalt molybdate sample produced slightly lower gas, higher coke and higher distillate yields. At high conversions, the yield of C_5 to 600°F product maintained a higher rate of increase per unit conversion increase than did the nickel molybdate sample.

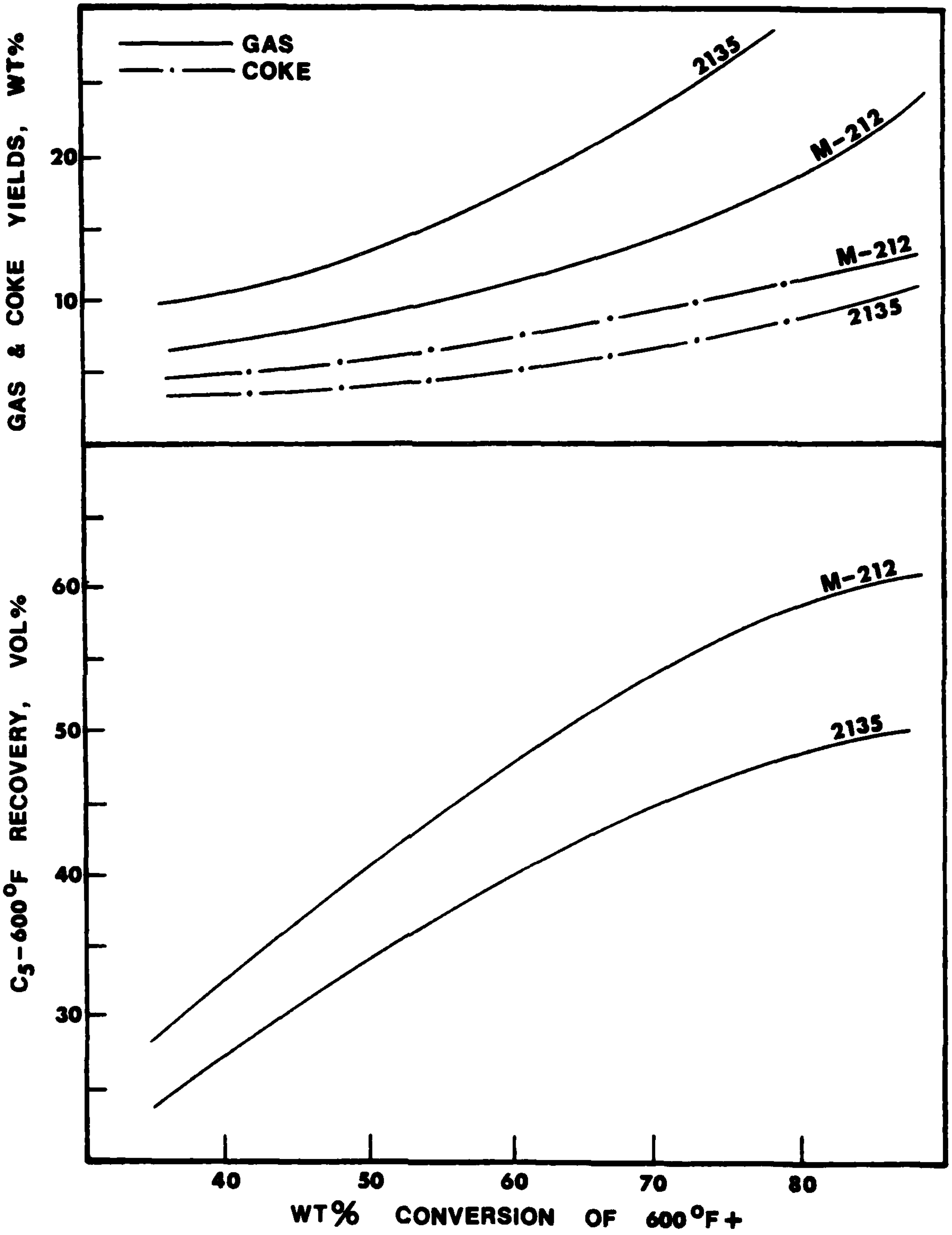


Figure IV-36. Comparison Of FCC Yields For A High Severity Hydrotreated Feed (2135) And A Low Severity Hydrotreated Feed (M-212)

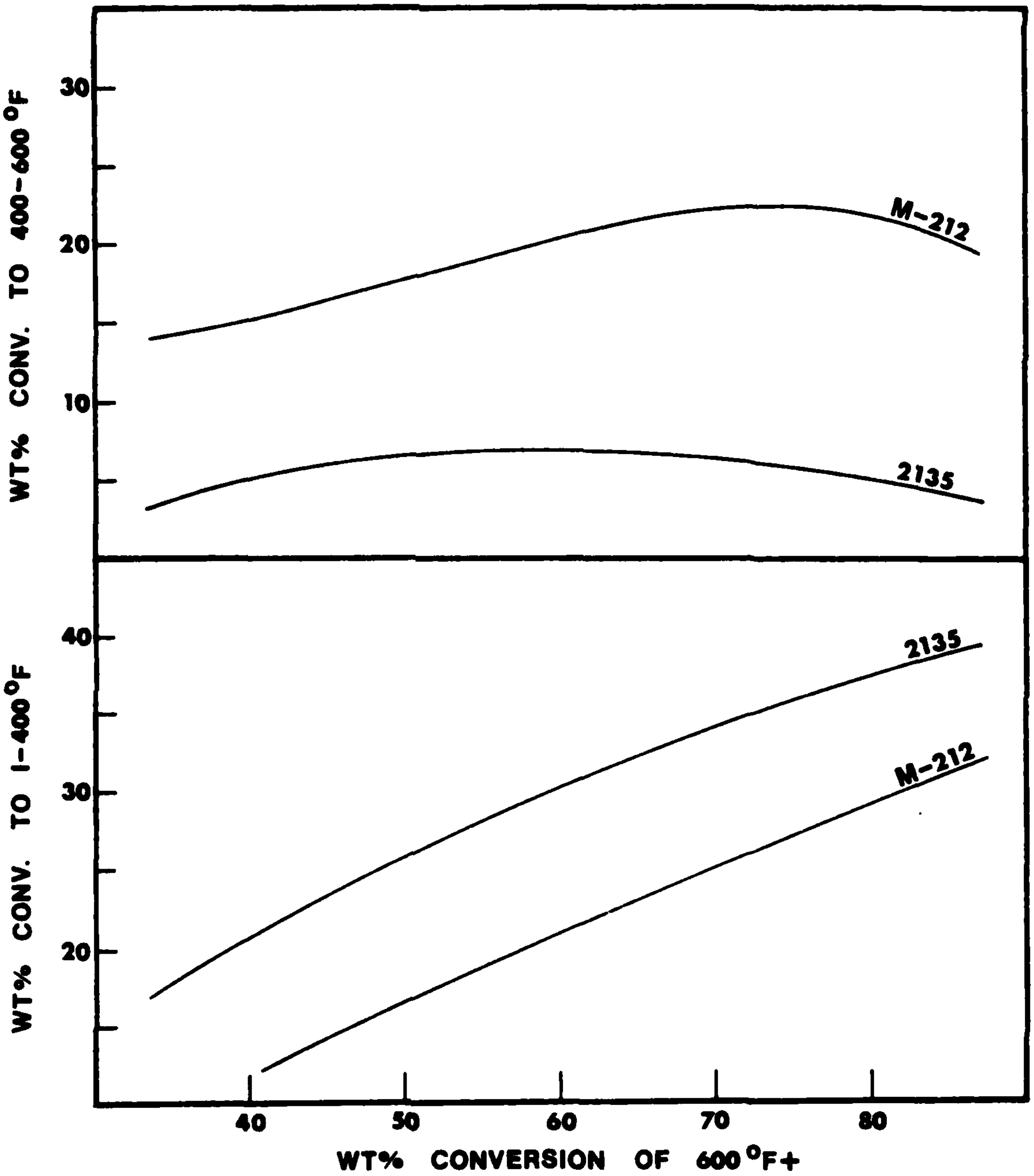


Figure IV-37. The Difference In FCC Yields For A High (2135) And A Low (M-212) Severity Hydrotreated Feedstock From Above-ground Shale Oil

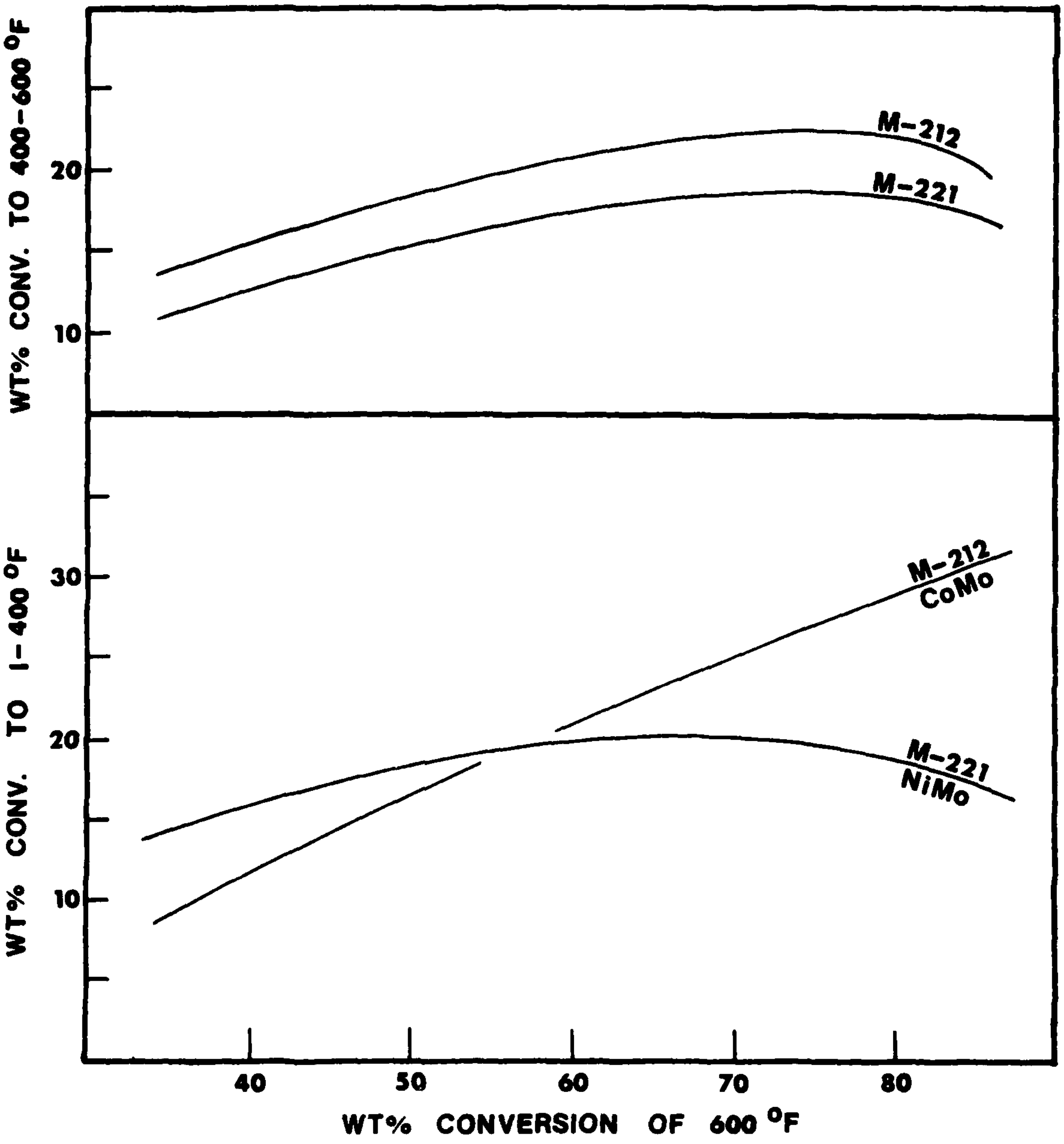


Figure IV-38. Comparison Of FCC Naphtha And Distillate Yields For Nickel And Cobalt Based Hydrotreating Catalysts

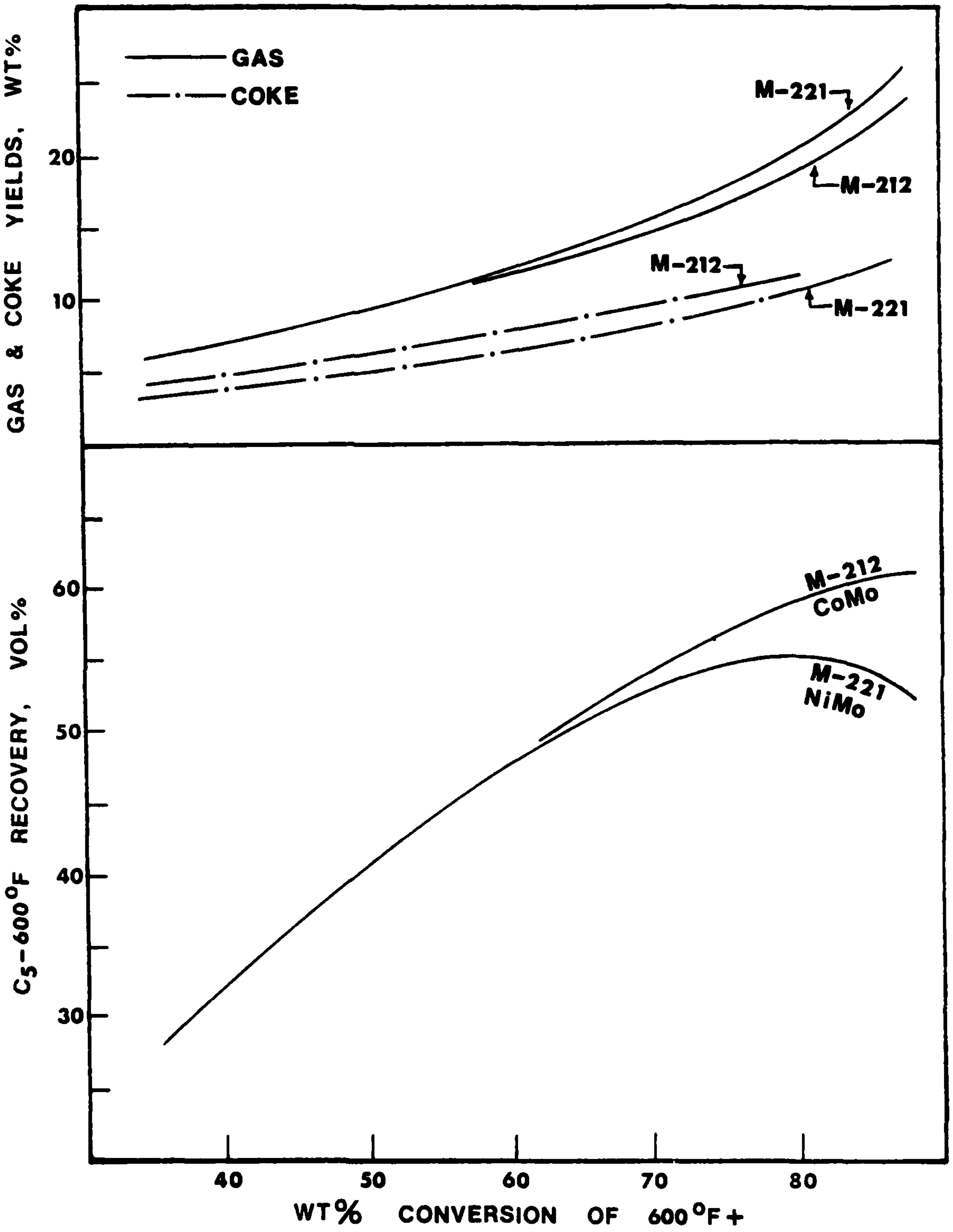


Figure IV-39. FCC Coke, Gas, And C_5-600°F Yields As A Function Of Hydrotreater Catalyst

Three recycle samples were evaluated - 500°F+ and 600°F+ original cobalt molybdate stocks and a 600°F+ original nickel molybdate stock. All materials had been hydrotreated over nickel molybdate catalyst in the recycle hydrotreater. Small differences were noted in gas and coke yields (Figures IV-40 and IV-41), but the differences in naphtha and distillate yields were significant. The 211 (500°F+) sample produced much higher naphtha and lower distillate yields. For plants where heavy fractions are in excess for turbine fuel blending, recycle of a 500°F+ material could be used to correct this problem with apparent good results.

As with the in situ material, larger samples were also processed on the circulating FCR unit. Results follow similar trends to those found for the in situ material, including, in particular, excessive coke yields.

Good denitrogenation was shown for all samples, although basic nitrogen removal was slightly lower than the in situ material. Hydrogen redistributions were obtained for feedstocks ranging 10.1 to 10.9 percent with product C_5 to 600°F distillate hydrogen contents ranging 12.1 to 12.7 and residuum about 11.3 percent. Again, sulfur levels in the products seem to approach limiting values.

Based on these results, there is very little apparent difference between the cobalt and nickel based hydrotreater stocks. Since the cobalt molybdate catalyst should provide lower denitrogenation and lower hydrogen consumption in the

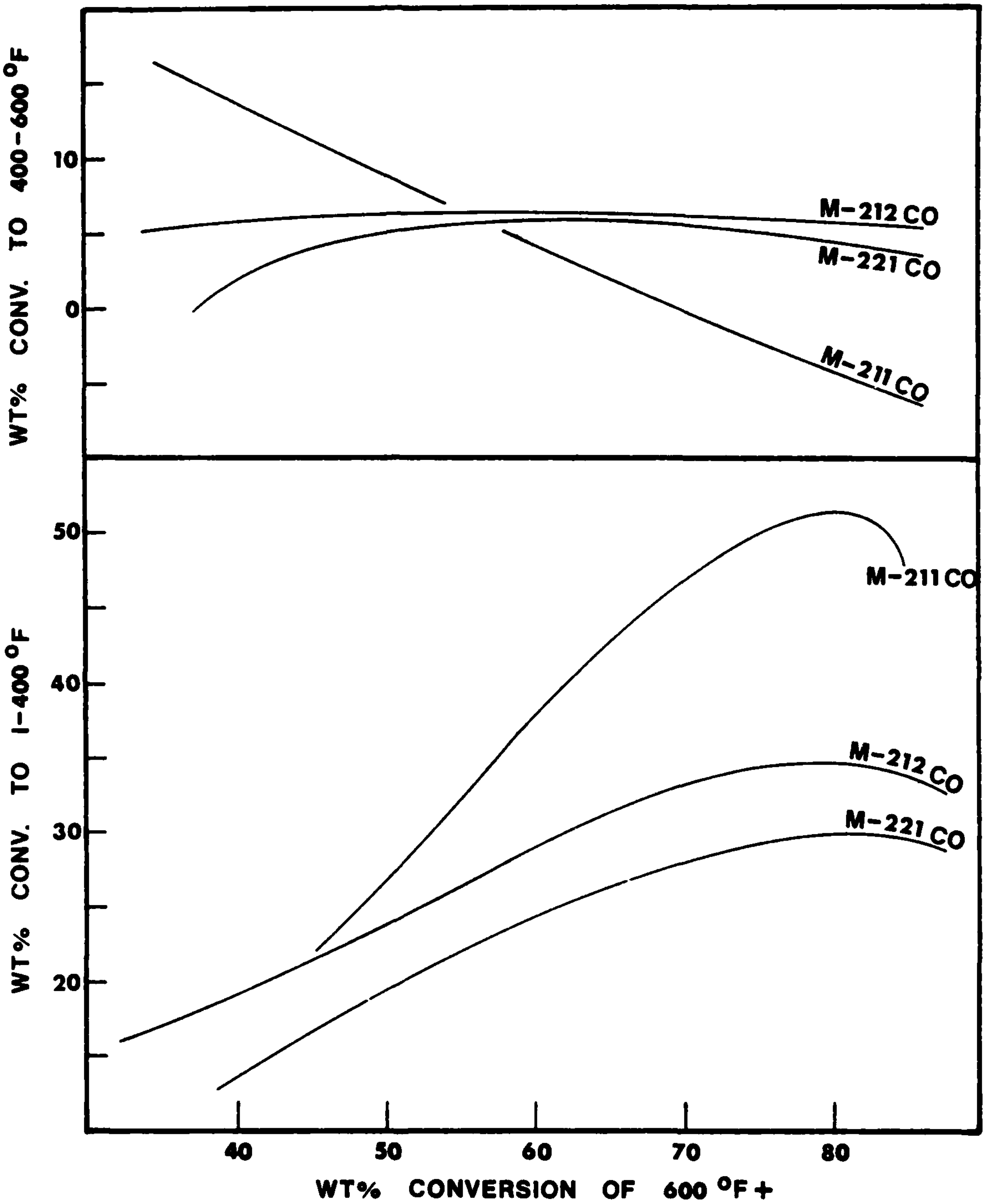


Figure IV-40. Effectiveness Of An FCC On Three Above-ground Shale Oil Streams Hydrotreated For Recycle

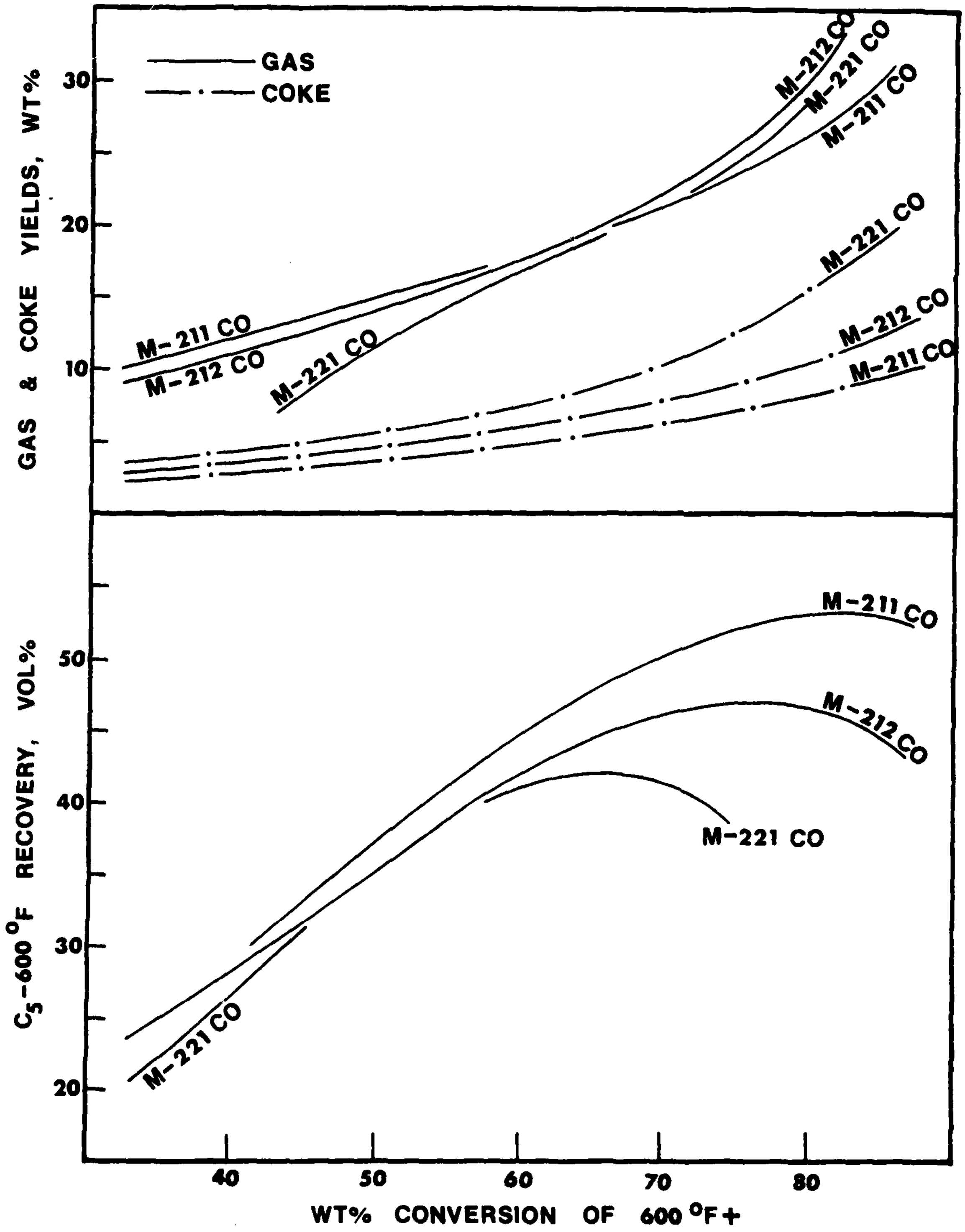


Figure IV-41. Breakdown Of Product Yields From FCC Operation On Three Samples Hydrotreated For Recycle hydrotreater, this option should provide least-cost results. As with the in situ material, full range feed to the FCC unit was shown to not be desirable.

COMPARISON OF FEEDSTOCKS

Figures IV-42 through IV-45 compare yield structures at comparable conversion for samples which were prepared in analogous manners. The results are startling. For samples prepared in an analogous manner, at equivalent conversions, the overall processability of the two oils are essentially analogous. C_5 to 600°F yields are essentially identical, and in fact, the nickel molybdate based samples fall on precisely the same curve (Figure IV-45). There are differences - the above-ground oil consistently produces slightly higher coke yields, lower gas yields, lower naphtha yields, and higher distillate yields. Overall, however, the oils are very comparable in terms of cracker feed quality. This result was <u>not</u> anticipated.

Finally, Figures IV-46 and IV-47 present desulfurization and denitrogenation during cracking. Surprisingly, relative nitrogen removal is independent of the source feedstock. Denitrogenation is a weak function of the quantity of catalyst contacted by the oil. Desulfurization, however, seems to follow a limiting value trend regardless of feed sulfur level, with a distinct difference between the source oils.

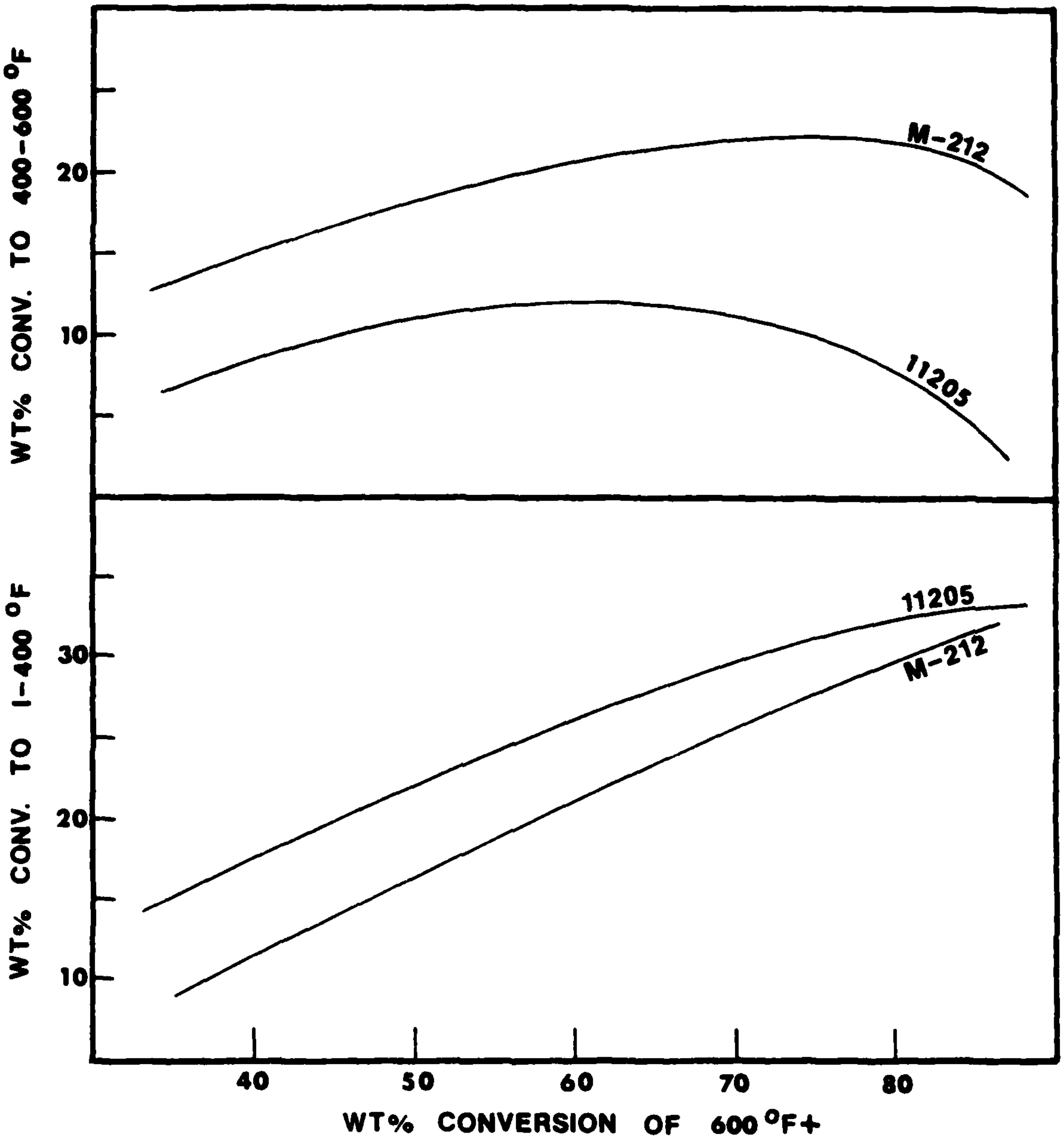


Figure IV-42. Comparison Of Yields From The Cracking Of An In Situ (11205) And An Above-ground (M-212) Shale Oil - Both Previously Hydrotreated Over Co/Mo Catalyst

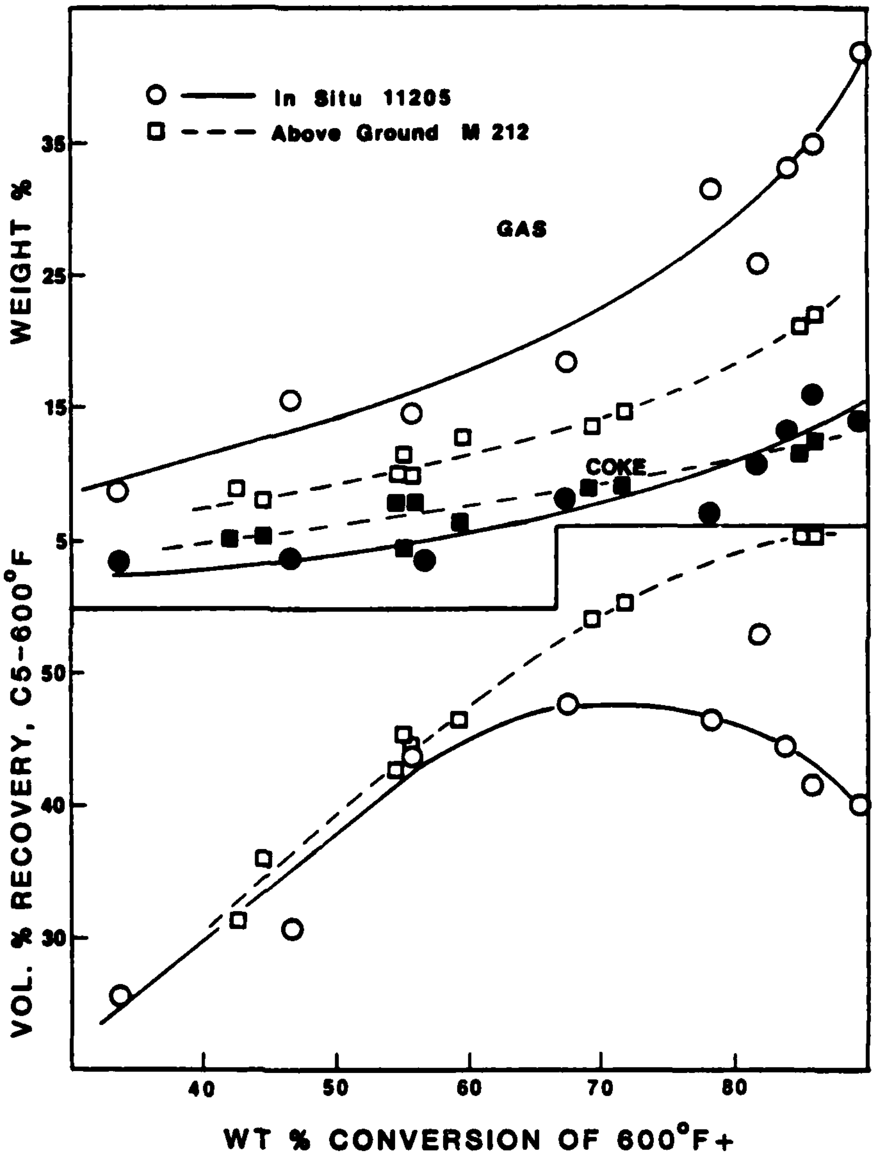


Figure IV-43. Cracking Of Two Cobalt Molybdate Hydrotreated Shale Oils

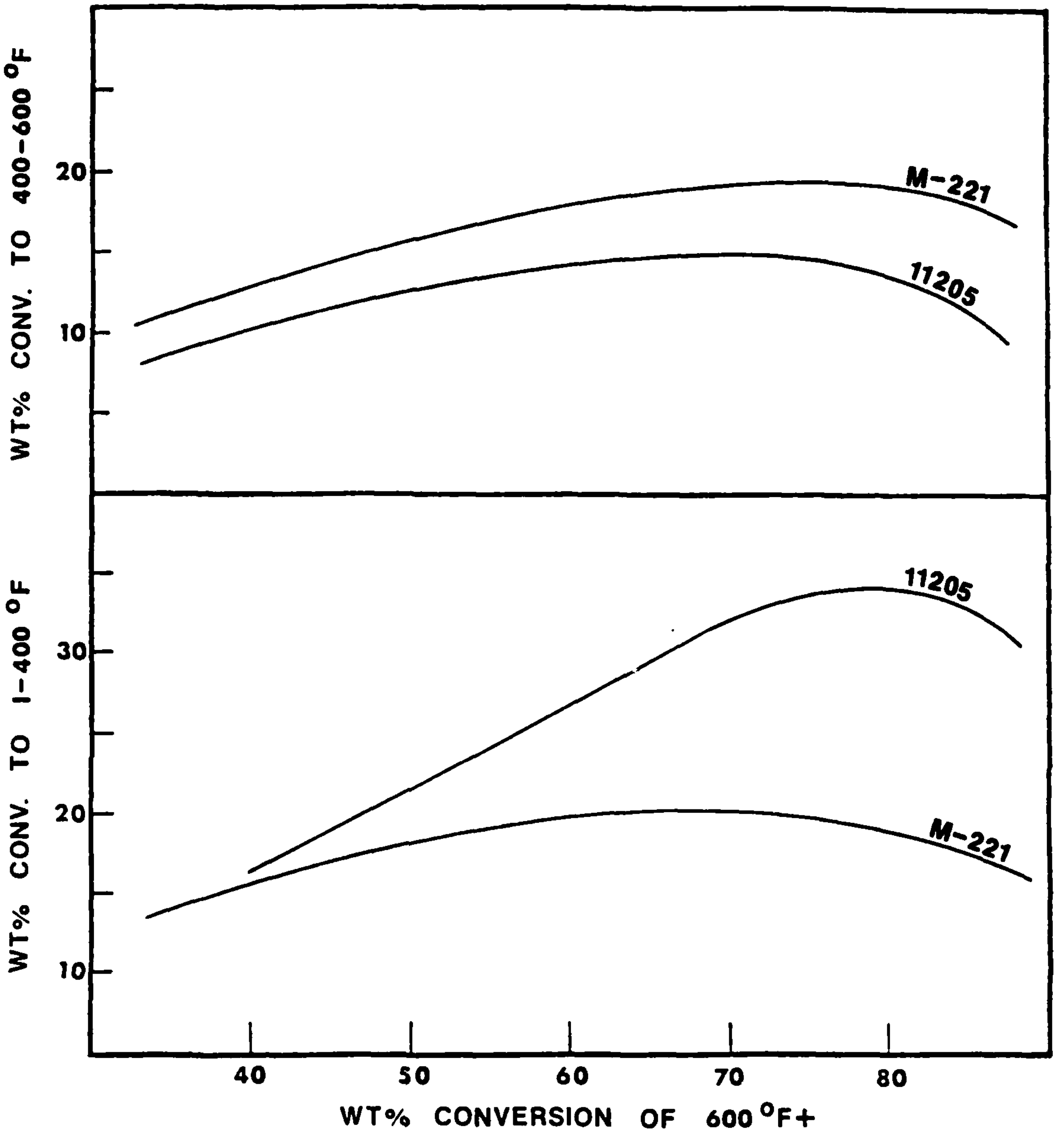


Figure IV-44. Comparison Of Naphtha And Distillate Yields From The Cracking Of An In Situ (12205) And An Aboveground (M-221) Shale Oil, Both Previously Hydrotreated Over Ni/Mo Catalyst

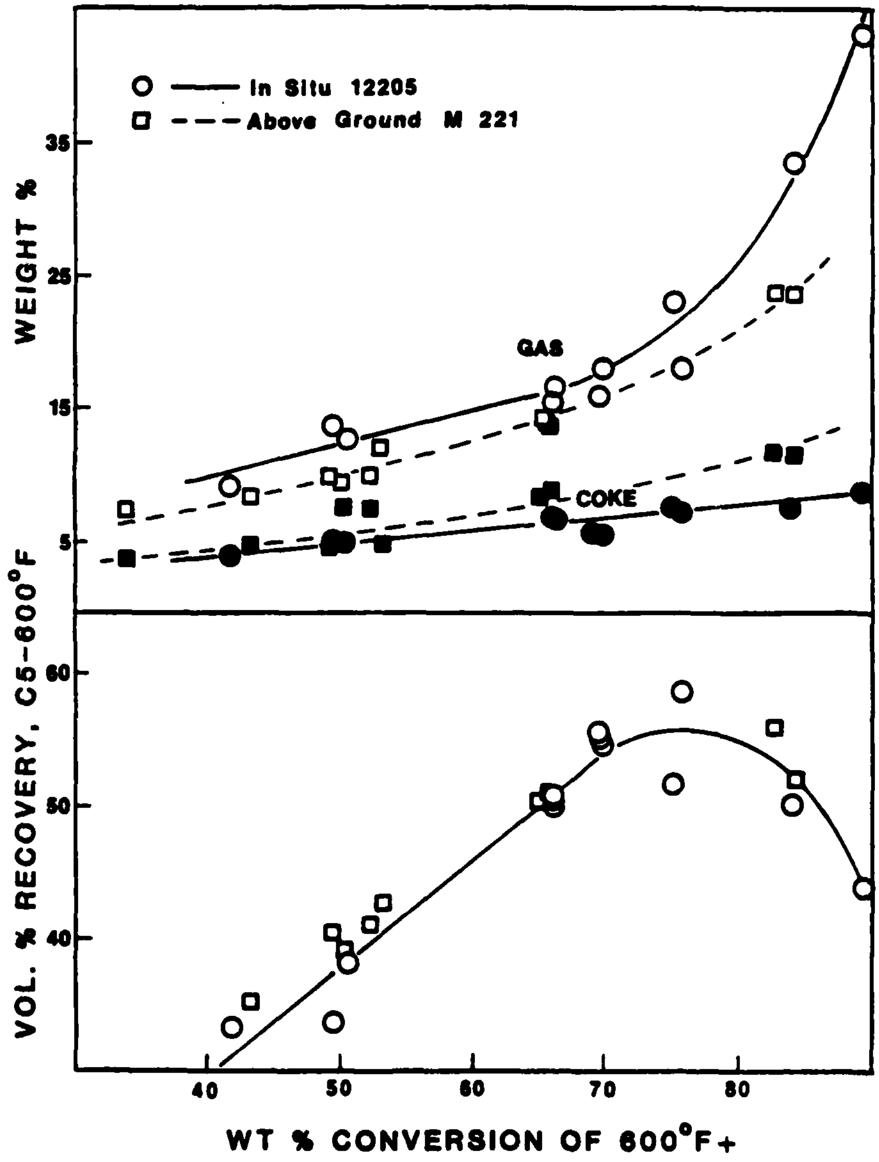


Figure IV-45. Cracking Of Two Nickel Molybdate Hydrotreated Shale Oils

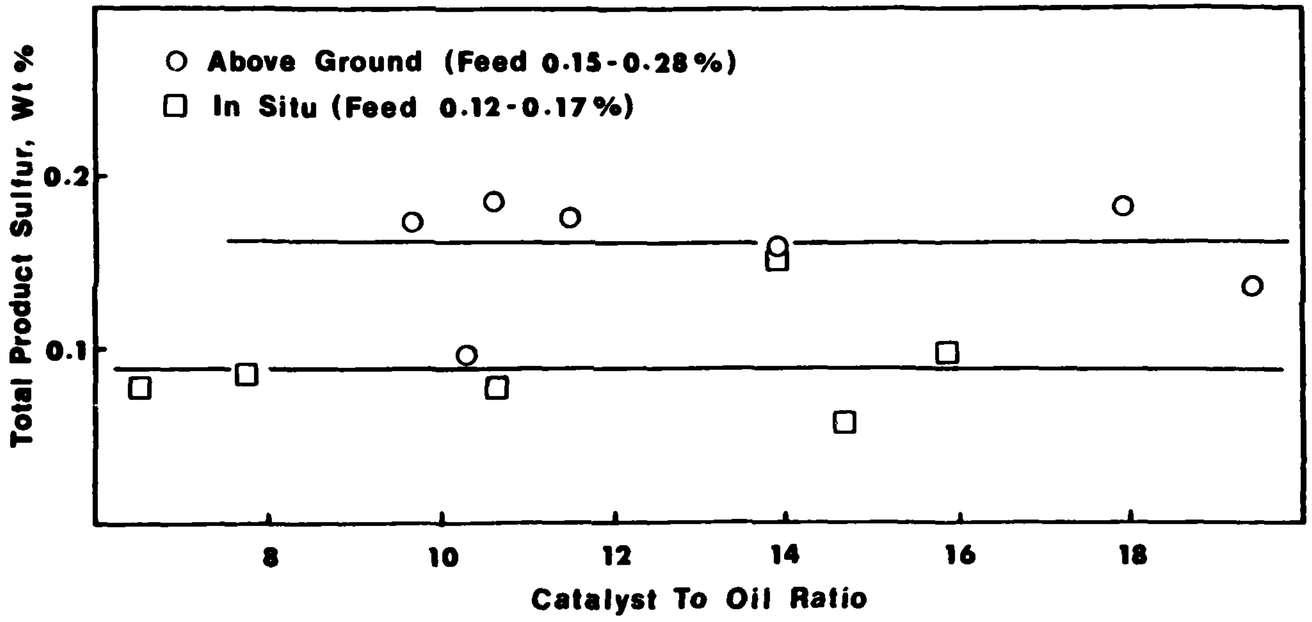


Figure IV-46. Desulfurization During Fluid Catalytic Cracking

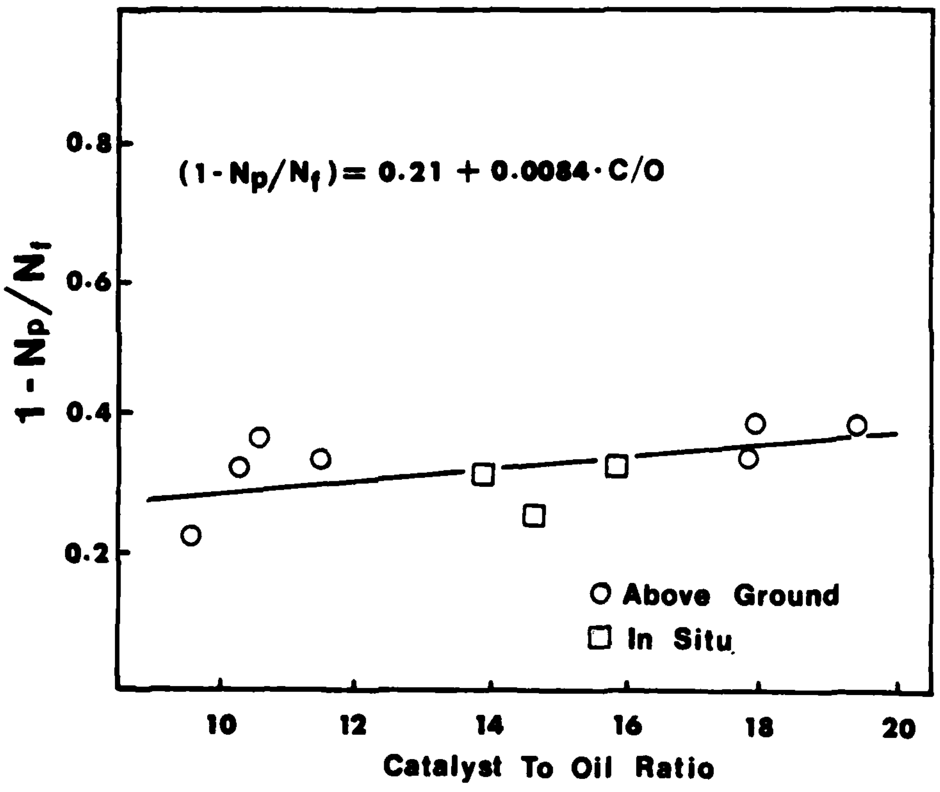


Figure IV–47. Denitrogenation During Fluid Catalytic Cracking

Both materials are acceptable EXTRACTACRACKING FCC feedstocks. Product quality of the above-ground oil is, however, lower than the in situ at comparable generation conditions in the hydrotreater.

4. Nitrogen Extraction. Nitrogen extraction is provided in the EXTRACTACRACKING process to allow denitrogenation without hydrogen consumption. Both batch and continuous countercurrent tests were provided in order to define required operating parameters and feedstock response. Table IV-4 keynotes this processing area.

IN SITU

Data developed during initial development of the EXTRACTACRACKING process prior to this contract had indicated that straight run hydrotreated distillate would probably be the most difficult product fraction to extract. As a result, this material was selected during Phase II for development of initial response data. Acid concentration, treating rate and number of stages were varied on a batch basis for this feedstock. As shown in Figure IV-48, higher strengths and dosages result in higher removal of basic nitrogen compounds. Minimum dosage requirements were defined by the observed decline in removal efficiency. A further consideration, however, is that total hydrocarbon removal should be minimized while maximizing nitrogen removal. Figure IV-49 demonstrates the material response in

TABLE IV-4

NITROGEN EXTRACTION

Objectives:	Remove significant quantities of nitrogen compounds without external hydrogen addition
Key Element:	Maximum nitrogen removal at minimum hydrocarbon loss
Parameters Evaluated:	• Feedstock genesis • Acid strength • Acid dosage • Temperature, viscosity
Unique Features:	• Nitrogen removal without hydrogen addition • Processing of high olefin stocks

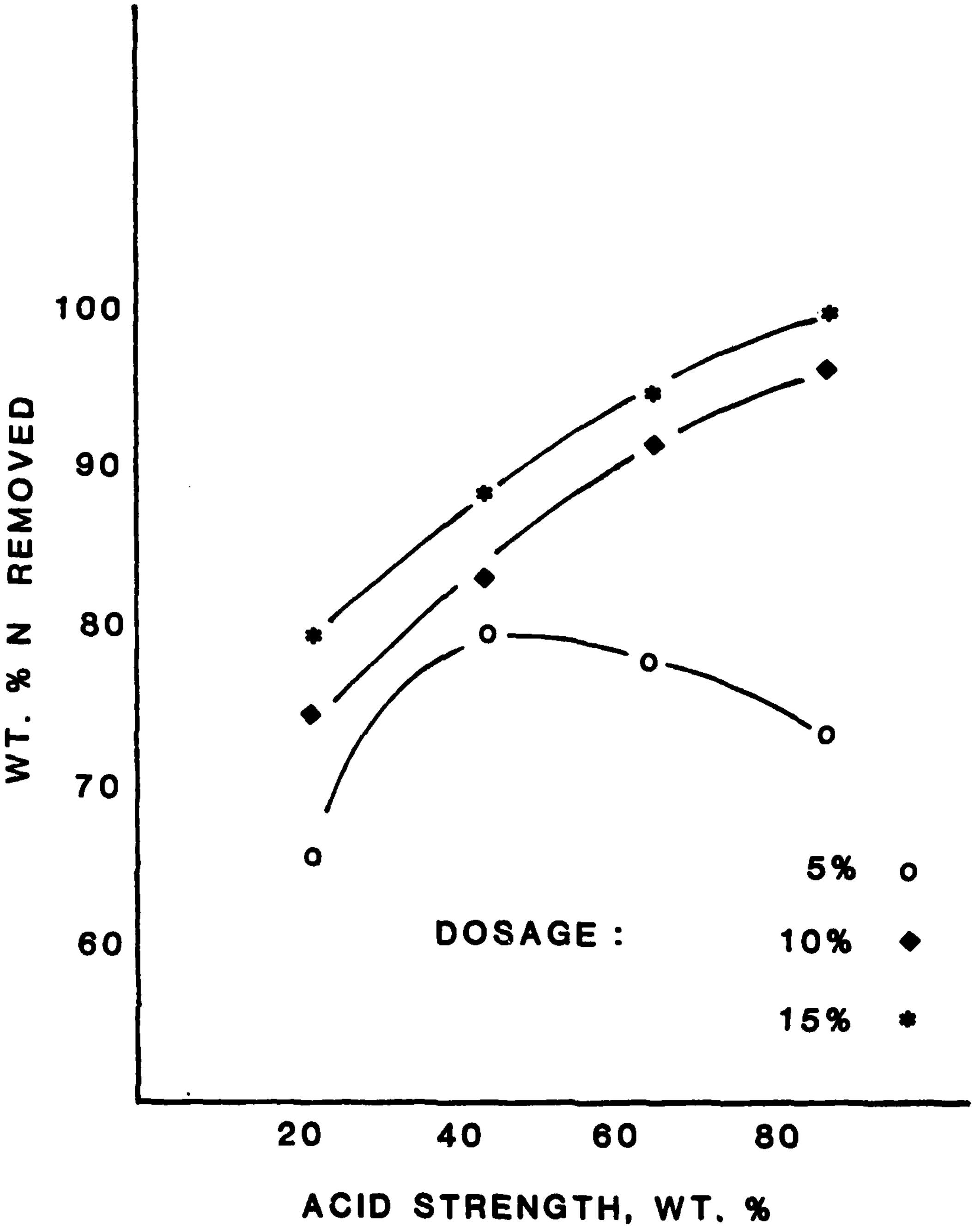


Figure IV-48. Batch Extraction Of Basic Nitrogen this manner. Rapid increases in hydrocarbon removal above about 45 percent, indicating removal of non-nitrogen compounds, place an upper bound on feasible acid strength.

These data defined the operating window for this unit. Continuous extraction operations were then performed on total (hydrotreated straight run plus catalytically cracked) C_6 to 600°F product. Figure IV-50 shows results from these continuous tests overplotted on the earlier straight run batch tests. As can readily be seen, the agreement is excellent.

Overall, the in situ nitrogen extraction work was very successful. Use of the parameters defined above resulted in basic nitrogen removals of 82.3 to 92.6 percent at hydrocarbon losses ranging 0.8 to 13.6 weight percent. Further data were also developed during these tests to allow detailed definition of the remaining process parameters for essentially any required feedstock.

Problems were encountered early in the continuous evaluations with raffinate contamination. As a result, a new product separation and clean-up system was developed and tested. Results were excellent, in that no measurable raffinate contamination was observed both in terms of product analyses and further processing module response.

Properties of the raffinates produced during these studies are shown in Table IV-5. Raffinate total nitrogen levels ranged from 0.20 to 0.24 weight percent, which is in excellent agreement with that predicted during Phase I.

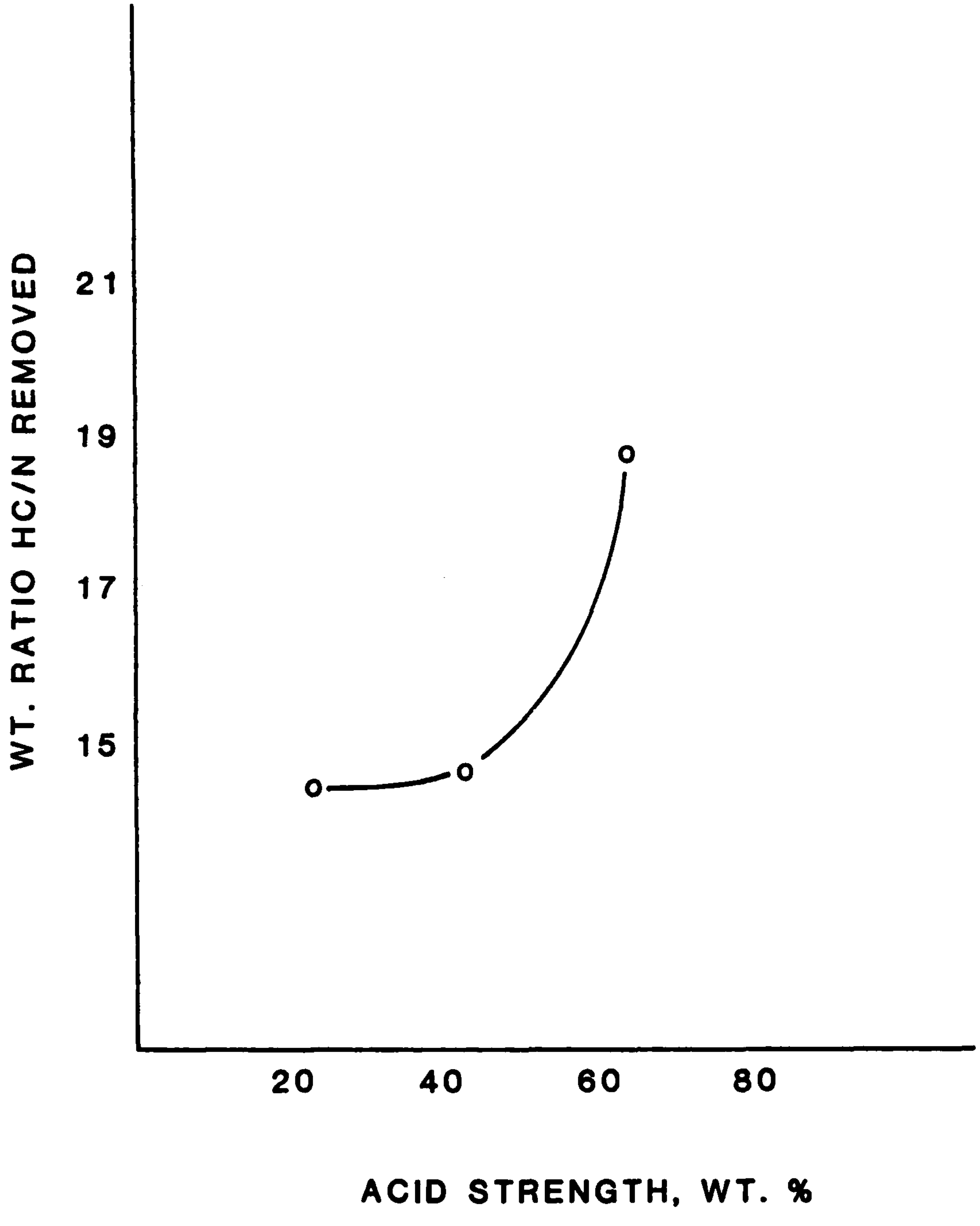


Figure IV-49. Ratio Of Hydrocarbon To Nitrogen Removal In Continuous Countercurrent Extraction

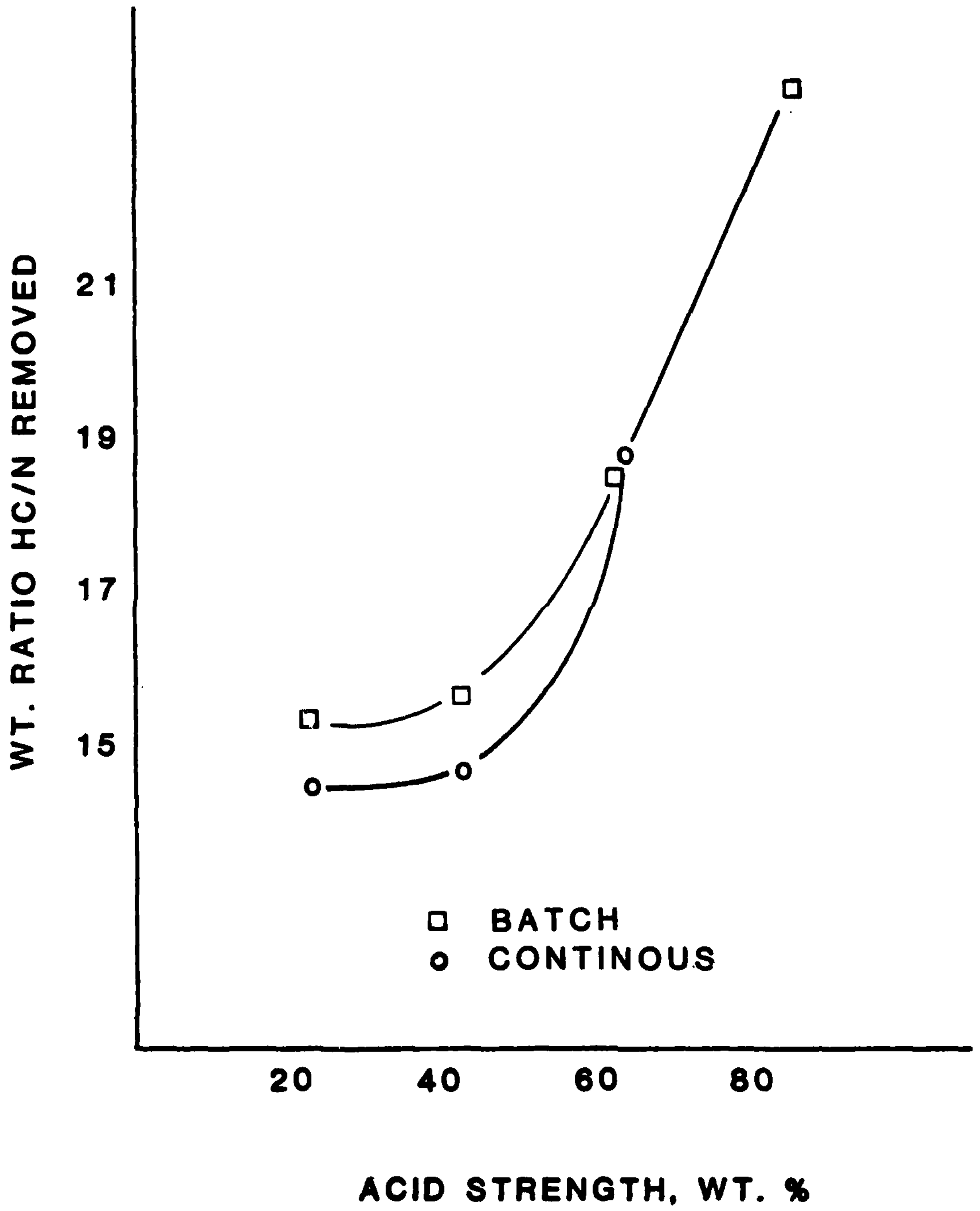


Figure IV-50. Comparison Of Batch And Continuous Extraction

TABLE IV-5

IN SITU FEED, RAFFINATE PROPERTIES

	M-112		M-121		GC-1							
					1		2		3		4	
	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE
API	38.0	39.6	38.5	40.0	36.6	37.3	36.0	37.6	36.5	38.1	40.9	40.2
BR NO.	42.0	39.3	42.2	45.0	38	42	41	43	46	37	52	47
S, WT, %	0.10	0.09	0.08	0.06	0.07	0.07	0.07	0.09	0.09	0.09	0.08	0.08
N(B), WT, %	0.700	0.0446	0.623	0.049	0.354	0.025	0.353	0.016	0.415	0.010	0.295	0.01
N REMOVAL, %	-	93.6	-	92.1	-	92.9	-	95.5		97.6	-	95.4
HC REMOVAL, %	-	7.5	-	9.5	-	9.9	-	5.4	-	3.2	-	0.8
SIM D, WT, %												
IBP	-	-	-	-	221	-	223	186	218	211	114	-
2	-	-	-	-	250	-	258	231	245	242	159	-
10	-	-	-	-	329	-	307	297	297	299	229	-
50	-	-	-	-	476	-	456	455	450	449	426	-
90	-	-	-	-	581	-	574	554	562	551	545	-
98	-	-	-	-	609	-	596	576	584	577	574	-
EP	-	-	-	-	682	-	658	582	646	602	586	-

Examination of bromine number and sulfur contents of the feed and raffinates confirm that essentially no problems were encountered with olefin or sulfur removal in the extract.

Extract properties evaluated during Phase II were also in agreement with Phase I estimates. API gravity ranged 13.8 to 14.0, sulfur content 0.03 to 0.13 weight percent, and the extract had a molecular weight of about 200. Elemental properties of the extract have also been developed to allow evaluation of various end uses of this material.

ABOVE-GROUND

Conditions developed for the in situ material were used for development of processing requirements for the above-ground material. There was excellent agreement in terms of anticipated processability of the two materials.

Properties of the extraction raffinates are shown in Table IV-6. Basic nitrogen removals ranged 72.6 to 99.1 weight percent at hydrocarbon removals of 6.1 to 14.4 weight percent. Raffinate total nitrogen content ranged from 0.26 to 0.45 weight percent. Problems with raffinate contamination were again encountered, which were solved in the same manner as for the in situ materials.

In order to examine potential olefin-based problems, separate straight run and catalytically cracked extractions were performed for two samples. In particular, the cracked

TABLE IV-6

ABOVE-GROUND FEED, RAFFINATE PROPERTIES

	M-212				M-221				GC-2							
	STRAIGHT RUN		CRACKED		STRAIGHT RUN		CRACKED		1		2		3		4	
	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE	FEED	RAFFINATE
API	35.6	39.4	40.7	42.4	37.0	40.6	42.0	44.0	36.9	39.3	38.5	39.8	36.7	39.5	41.7	41.3
BR NO.	29	28	101	89	27	25	104	99	62	51	52	51	53	60	54	46
S, WT, %	0.17	0.18	0.21	0.21	0.15	0.18	0.16	0.15	0.14	0.13	0.14	0.13	0.18	0.18	0.21	0.20
N(B), WT, %	1.14	0.31	0.78	0.42	1.07	0.18	0.74	0.03	0.646	0.021	0.585	0.005	0.795	0.023	0.802	0.089
N REMOVAL, %	-	72.6	-	94.6	-	83.3	-	95.8	-	96.8	-	99.1	-	97.1	-	88.9
HC REMOVAL, %	-	14.8	-	4.4	-	14.3	-	4.3	-	8.6	-	11.0	-	8.3	-	8.9
SIM D, WT, %																
IBP	-	-	-	-	-	-	-	-	184	-	177	156	171	143	123	-
2	-	-	-	-	-	-	-	-	219	-	220	207	201	178	161	-
10	-	-	-	-	-	-	-	-	292	-	291	286	325	281	237	-
50	-	-	-	-	-	-	-	-	439	-	426	435	467	448	423	-
90	-	-	-	-	-	-	-	-	555	-	525	543	578	559	545	-
98	-	-	-	-	-	-	-	-	610	-	575	573	595	577	579	-
EP	-	-	-	-	-	-	-	-	685	-	605	585	660	587	649	-

chargestocks demonstrated bromine numbers over 100. No operating problems were encountered with either sample. In fact, the cracked samples proved to be better extraction feedstocks than the straight run materials. This is at least due in part to the boiling range distribution differences between the materials.

Extract properties were similar to those found for the in situ materials when nitrogen level, boiling range and source characteristics are considered.

COMPARISON OF FEEDSTOCKS

Comparative extraction response of these materials is remarkably similar. While higher nitrogen levels are encountered with the above-ground material and several boiling range differences occur when different source materials are charged, percent response factors are very consistent. Feedstock nitrogen content and boiling range distribution are sufficient information to define required operating parameters, chargestock response and product properties. Both materials are excellent extraction chargestocks when properly prepared in the hydrotreater and FCC units.

5. Recycle Hydrotreating. Recycle hydrotreating is provided for the EXTRACTACRACKING process in order to produce an improved recycle feed stream to the FCC unit. Due to volumetric considerations, even high hydrogen consumption in this unit is of minor importance when compared to

producing a similar material directly from the crude shale oil hydrotreater. Further, the materials have been upgraded twice, and are actually better hydrotreater feedstock than the original shale oil. Upgrading prior to recycle allows much higher conversions per pass through the FCC unit without excessive gas and coke production. Process keys are shown in Table IV-7.

Whether this module will be used in the EXTRACTACRACKING process is, at present, indeterminate, primarily due to mechanical and cost considerations. Work in Phase III will further define the relative desirability of this option. Obviously, particulate contamination from the FCC unit poses a severe problem for a fixed bed hydrotreating unit. Options for addressing these problems are available through present commercial applications of upflow, rather than downflow, hydrotreating, particulate separation, partition of particulates during fractionation and/or any combination of these or other factors. Obviously these items cannot be addressed in micro laboratory units. For that reason, utilization of the recycle hydrotreater will be determined as noted above based on pilot plant data and relative cost evaluation during Phase IV.

Data derived during Phase II address two major factors: (1) hydrotreating response, assuming that the material is able to be processed and (2) the effect of hydrotreating on recycle crackability. The FCC response data have been presented in Part 3.

TABLE IV-7

RECYCLE OIL HYDROTREATING

Objectives: Upgrade heavy FCC products to improve recycle crackability

Key Element: Product response to cracking

Parameters Evaluated:

- Feedstock source
- Operating severity

Unique Features:

- Hydrotreatment prior to recycle
- Conditions correspond to present commercial practice

Figures IV-51 and IV-52 present hydrotreating response data for this material. The curves are conventional, within the ranges of expected behavior. The primary result from these data, in addition to developing a response matrix for evaluation, lies in comparing these responses to that obtained in the crude shale hydrotreater. As shown in Figure IV-51, desulfurization of these materials is significantly more difficult than observed in the crude hydrotreater. Apparently, the residual sulfur compounds in the FCC bottoms are considerably more refractory to hydrotreating than those in the original material. This is not unexpected, and may be due to the particular sulfur species remaining.

Somewhat surprisingly, however, the nitrogen compounds in this material appear to be of no significant difference from those found in the crude shale oil in terms of hydrotreating response. The minor differences shown in response data (Figure IV-52) are directly attributable to catalyst type and a slight difference in operating pressure. These data may portend further avenues of research into both the types of nitrogen compounds found in shale oil and their relative response to processing.

6. <u>Guardcase Processing</u>. In general, the combination of hydrotreating, catalytic cracking and extraction provides a feedstock for upgrading to liquid transportation fuels which is relatively independent of source oil. Experimentation performed for this plant section was based on the

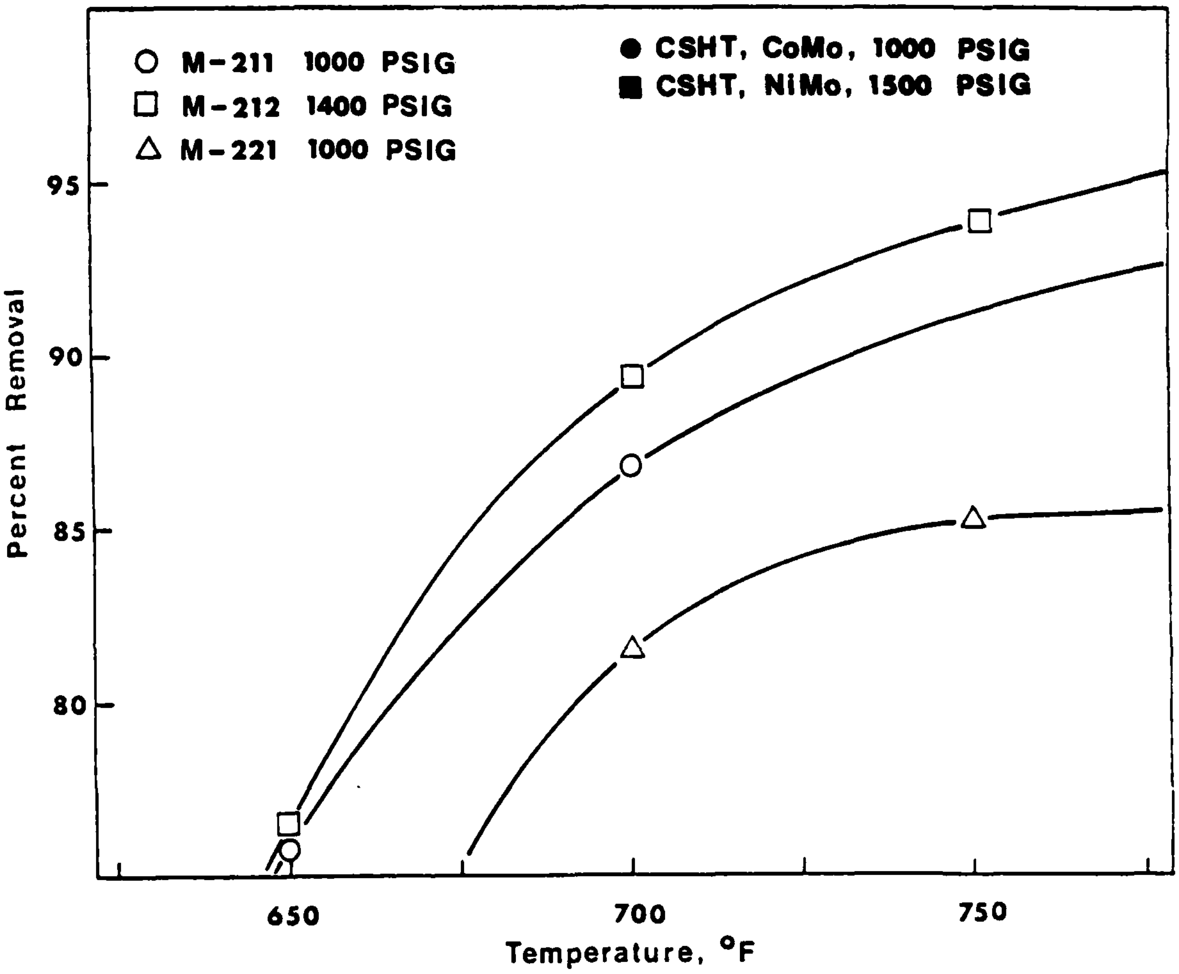


Figure IV-51. Cycle Oil Hydrotreating – Above-ground Shale Oil – Temperature Dependence Of Desulfurization At 1 LHSV

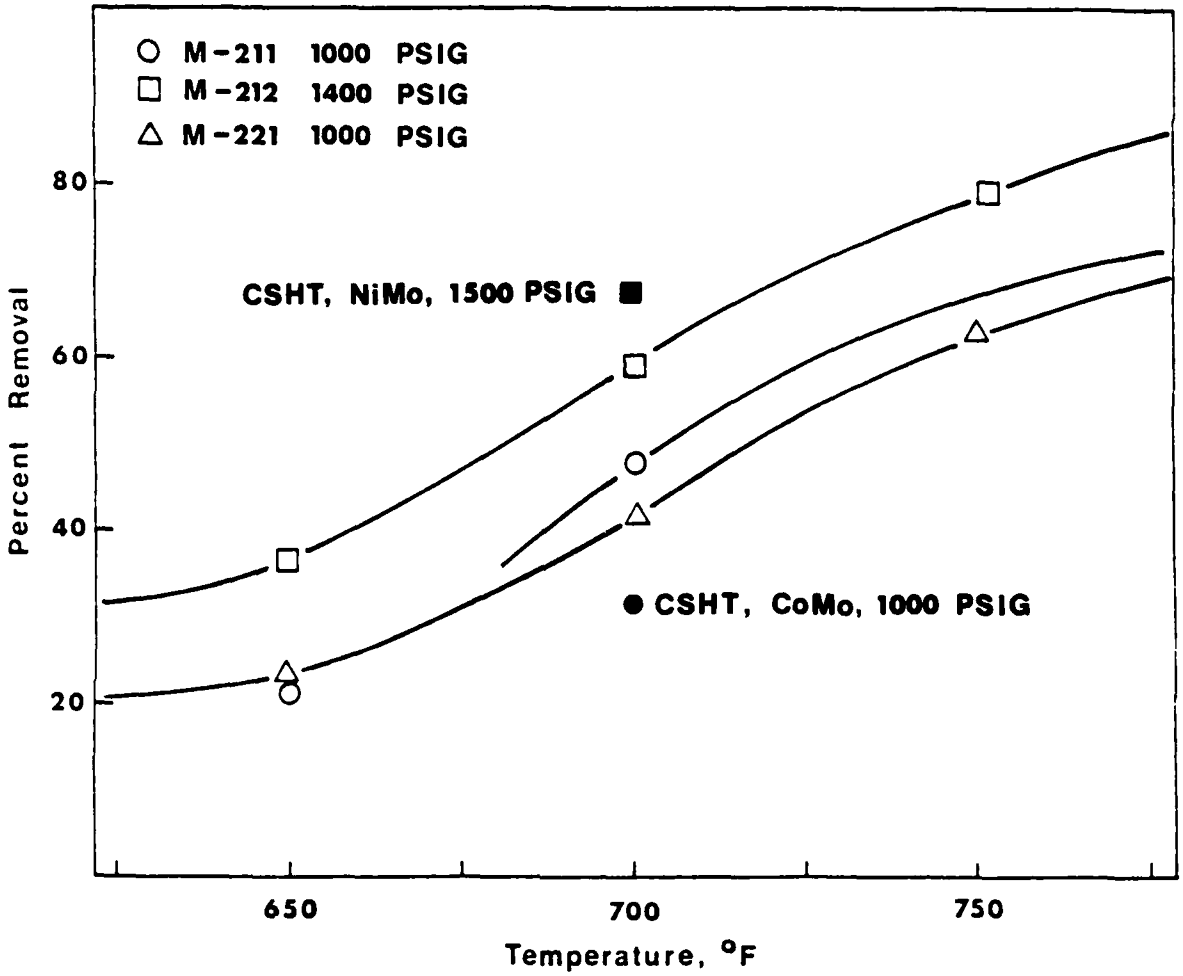


Figure IV-52. Cycle oil Oil Hydrotreating - Above-ground Shale Oil - Temperature Dependence Of Denitrogenation At 1 LHSV targeted fuel sample produced and was designed to define operating characteristics required for each material. Process keys are shown in Table IV-8.

IN SITU OIL

Three in situ samples were evaluated in the guardcase module. Two samples demonstrated unacceptable performance and required two-stage hydrotreating. This requirement was later shown to be due to contamination from the extraction process. The third sample, produced with an improved raffinate clean-up, was processed successfully at conditions analogous to that projected during Phase I.

Products from the guardcase operation were remarkably similar, particularly in light of the different fractionations practiced. Sample M-112 was designed to produce JP-4, M-121 to produce JP-8 and GC-1 to produce a combination of potential turbine fuels. Regardless of these differences, the guardcase products after fractionation demonstrated comparable aromatic contents (23 to 30 percent), and API gravity (39.1 to 43.7). Freeze points were also similar, being -31°F for GC-1, -34°F for 121 and -56°F for 112, with the key similarity being a nominal 20°F differential from the required target turbine fuel specifications. These properties, in particular freeze point, are in agreement with Phase I predictions.

TABLE IV-8

GUARDCASE HYDROTREATING

Objectives:	Process the extraction raffinate to a quality suitable for further upgrading: remove final traces of heteroatoms, metals, etc., as necessary.
Key Element:	Product suitable for use as reformer charge
Parameters Evaluated:	• Feedstock source • Operating severity
Unique Features:	• Feedstock end point

ABOVE-GROUND

Similar processing experience, problems and solutions were encountered for the above-ground feedstocks. Product aromatics ranged 17 to 20 percent, gravities 45 to 48° API and freeze points -35 to -52°F. Again, these properties are dependent on targeted fuels, and again, a nominal 20°F freeze point differential compared to specification was obtained.

COMPARISON OF OILS

Table IV-9 delineates required processing severity defined for these materials. There is a marked decrease in severity requirement for the materials processed with the new clean-up system (GC-1 and GC-2). These data also indicate that slightly higher severities are required for the above-ground than for the in situ materials.

Product properties indicate that the above-ground materials, after guardcase hydrotreating, are slightly superior to the in situ samples processed. The majority of this difference, however, is probably due to the sample production conditions used prior to the guardcase and the slightly higher guardcase severity provided.

7. Freeze Point Modifications. As demonstrated in the previous section, blending of all potential turbine fuel boiling range material to finished turbine fuels is not possible for these stocks due to nominal 20°F shortfalls

TABLE IV–9

APPARENT MINIMUM SEVERITY REQUIREMENTS GUARDCASE HYDROTREATING

Shale Oil Type	Sample Number	Feed Nitrogen Wt %	Temperature °F	Pressure PSIG	LHSV Hr^{-1}
In Situ	M-112	0.24	700	1200	0.6
	M-121	0.23	700	1200	0.65
	GC-1	0.20	650	1000	1.0
Above Ground	M-211	0.36	700	1200	0.94
	M-212	0.45	725	1200	0.93
	M-221	0.34	700	1200	0.49
	GC-2	0.26	650	1200	0.96

when comparing observed freeze points with required specifications. Freeze point modification is provided to increase the percentage of material which can be blended to turbine fuel. Samples evaluated were again those targeted for final fuel sample production. Early in the program, however, simulated feedstocks were processed for a complete range of response data and processing conditions defined based on those data. An overview of this module is shown in Table V-10.

IN SITU

The three in situ samples described in Part 6 were subjected to freeze point modification at conditions estimated to be near optimum from the simulation studies. Freeze point depressions of 23, 12 and 18°F were obtained with aromatic content increases of 20, 20 and 19 volume percent for samples 112, 121 and GC-1, respectively. While aromatic response was remarkably similar, the freeze point depressions were not. Examination of all data indicates the primary functionality to be the boiling range distribution. In the order 112 ⟶ 121 ⟶ GC-1, mid-boiling point increases 15°F per sample and end point also increases correspondingly. Therefore, control of the freeze point modification process must include not only aromatics but also relative boiling range distribution, with the heavier materials being of apparent equal processability

TABLE IV-10

FREEZE POINT MODIFICATION

Objectives: Reduce the freeze point of the guardcase products to maximize the quantity of the desired turbine fuel fractions. Concurrently, upgrade the produced gasoline (if any) octane number.

Key Element: High end point reforming

Parameters Evaluated:
- Feed source
- Boiling range
- Operating severity

Unique Features:
- High end point reforming
- Concurrent freeze point depression and octane improvement

(in terms of aromatics), but conversely offering a lower freeze point improvement per incremental aromatic increase.

An accelerated aging test was performed for the GC-1 sample, as shown in Figure IV-53, to determine the impact of the relatively high feedstock end point. While deactivation did occur, a loss of freeze point depression activity of only 1°F was observed for a time period which would correspond to roughly two months operation in petroleum naphtha. This deactivation rate was determined to be acceptable.

ABOVE-GROUND

The above-ground samples were again very similar in response to the in situ materials. Four samples were processed: 211, 212, 221 and GC-2, as produced in the guard-case module. All were similar with the exception of 211, which had a lower end point than the other materials. Freeze point depressions of 15, 13 and 20°F were obtained for samples 211, 212 and GC-1, at aromatic increases of 23, 19 and 20 percent, respectively. There was not as strong a boiling range functionality as for the in situ material, although the relative ranking of freeze point depression was 13, 15, and 20°F corresponding to mid-boiling points (by simulated distillation) of 398, 385 and 406°F, respectively.

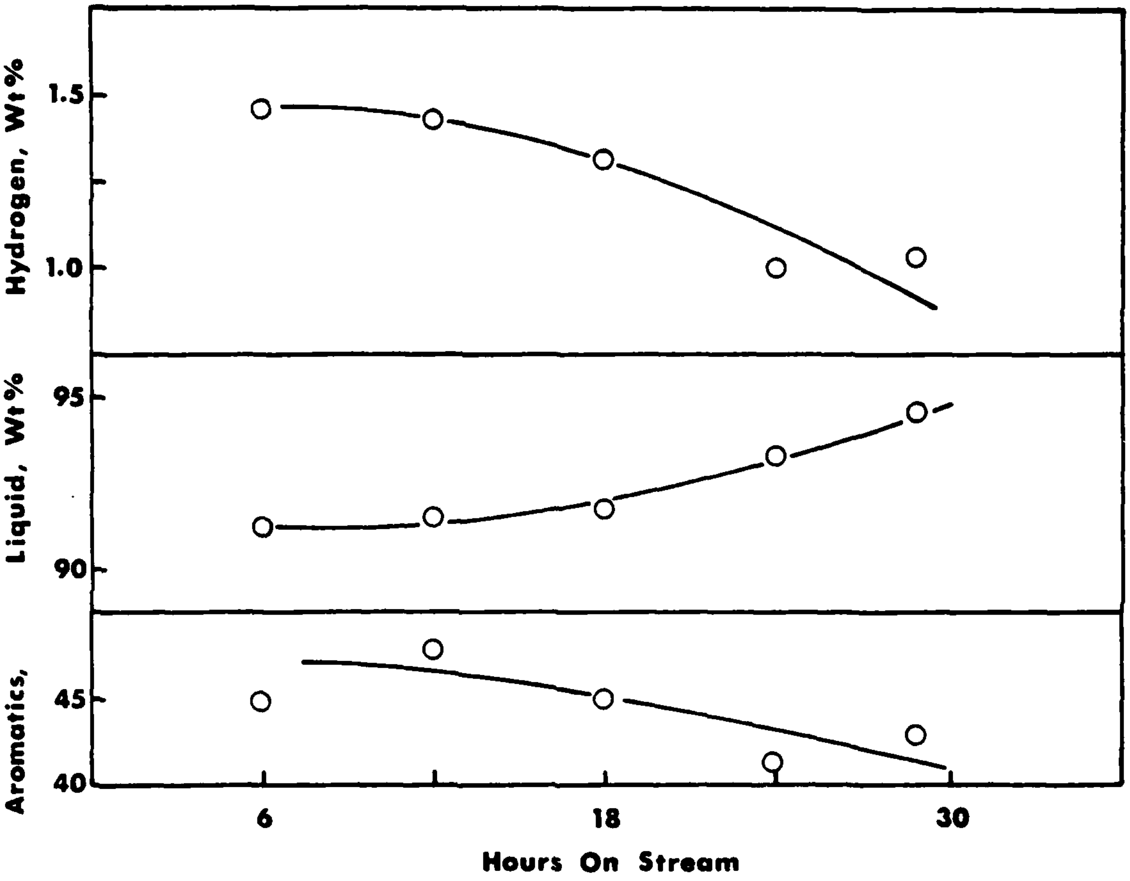


Figure IV-53. Accelerated Aging Response Of Sample GC-1 (Normalized Data)

An accelerated aging test was also performed for the GC-2 sample, as shown in Figure IV-54. Relatively high deactivation rates were encountered which would require either slight processing condition modification or use of a continuous regeneration unit. While the required changes are not anticipated to be major, the product response at the conditions used was unacceptable.

OIL COMPARISON

The in situ material appears to be slightly more responsive per incremental aromatics change to freeze point depression. However, all products demonstrated very similar properties within a narrow range of values. While the targeted 20°F or greater freeze point depressions were attained for only two of the seven samples, significant changes were provided for each sample. There appears to be a lower response for the shale-derived materials than the simulated materials, which might be expected due to the extremely high freeze points of the simulated stocks. Processing conditions were deemed adequate for the in situ material, but slight changes will be required for the aboveground material to increase cycle lengths.

8. Aromatic Saturation. Aromatic saturation is provided to reduce high aromatic levels produced during freeze point depression to acceptable levels. Each of the samples processed as described in Parts 6 and 7 were routed through

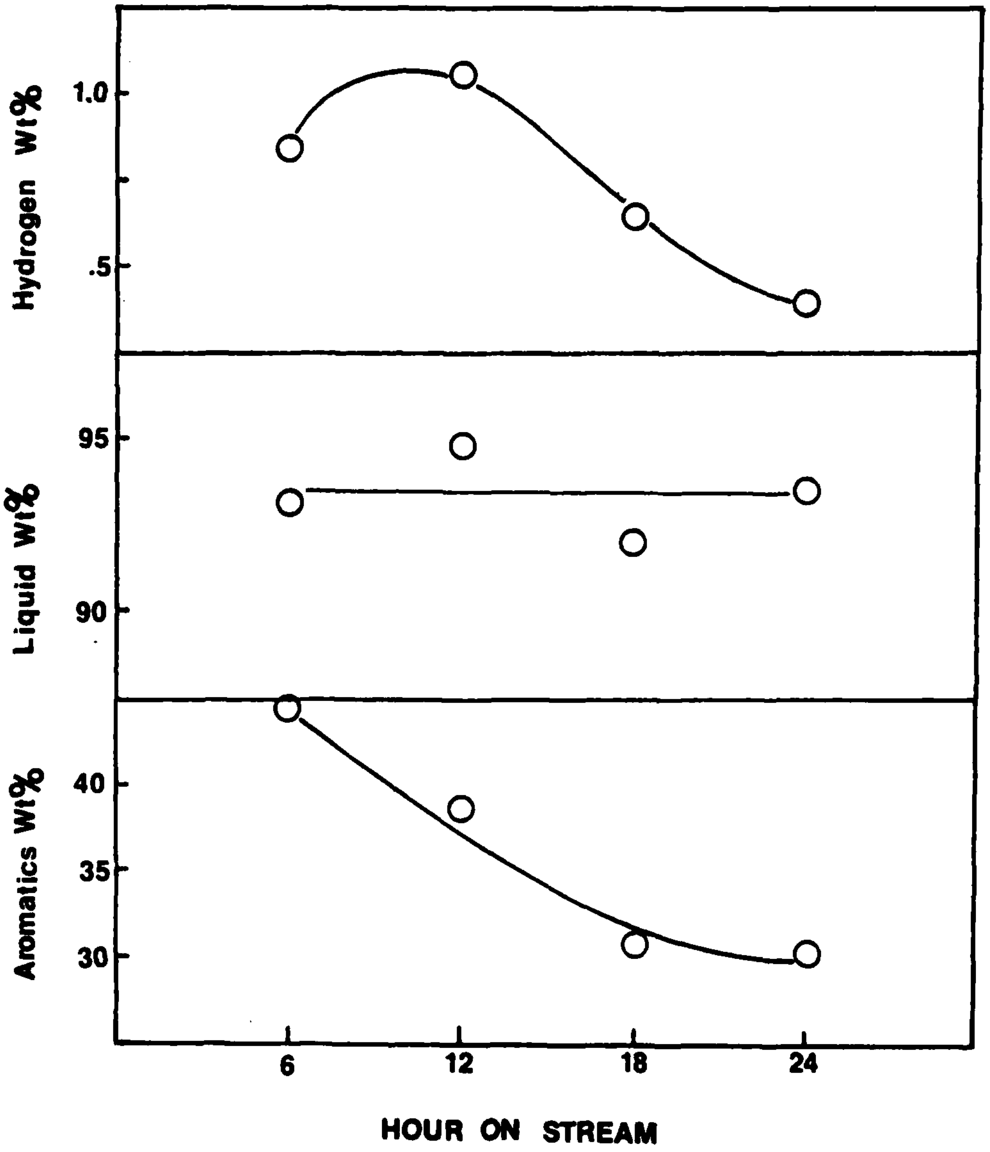


Figure IV-54. Accelerated Aging Response Of Sample GC-2 (Normalized Data) the saturation unit. Samples 121 and 211 were fractionated to provide a nominal +300°F (ASTM) feedstock. All samples were processed under analogous conditions. Table IV-11 presents a module overview.

Results were somewhat surprising. All feedstocks demonstrated aromatic contents of roughly 40 ± 2 percent. However, product aromatic contents ranged from 6 to 33 percent, with no direct explanation for this wide range of values available. Minor condition changes are probably required for this unit, but these are items of minor consequence.

TABLE IV-11

AROMATIC SATURATION

Objectives:	Reduce turbine fuel aromatics content to acceptable levels
Key Element:	Aromatic saturation to less than 25%
Parameters Evaluated:	• Feed source
Unique Features:	• Application to this use

SECTION V

SAMPLE PREPARATION - TASK II

As noted in previous sections, preparation of five 500 milliliter military turbine fuel samples were required during this study. Further, where possible, these samples were to demonstrate varying quality characteristics. Also, as noted previously, in many cases these samples were prepared concurrent with the Phase II parameter screening studies.

During the program, experimental studies were designed to produce finished fuel samples based on both 5-day and extended 30-day crude shale oil hydrotreating studies. Table V-1 delineates the major program increments designed for sample production and the key parameters utilized.

Each of these materials was processed completely through the EXTRACTACRACKING plant with the exception of recycle oil cracking. This portion of the process was not provided due to time and complexity constraints and the availability of time for this portion of work during the larger Phase III sample production efforts. Selected samples were processed for data, however, through both recycle oil hydrotreating and cracking. Actual processing results, sample documentation and calculated as-produced and with recycle yields are presented below for each sample. Methods used for evaluating the properties of each turbine fuel sample are shown in Table V-2.

TABLE V-1

PROGRAM DESIGN FOR 500-MILLILITER FUEL SAMPLE PRODUCTION

SERIES		ORIGINAL TURBINE FUEL MODE	KEY PARAMETERS
IN SITU	ABOVE-GROUND		
M-112	M-212	Blocked-out	The source oil was hydrotreated over cobalt molybdate catalyst. The entire 5-day product composite was fractionated to 600°F atmospheric overhead
M-121	M-221	Blocked-out	Same as M-112 and 212, except hydrotreated over nickel molybdate catalyst
GC-1	GC-2	Concurrent Production	The source oil was hydrotreated over cobalt molybdate catalyst for a period of 30 days. Selected product composites were stabilized with the FCC feed utilized being <u>non-fractionated</u> material

TABLE V-2

AVIATION TURBINE FUEL TEST METHODS

Description	Method
Gravity, API	ASTM—D287
Hydrogen	ASTM—D3701
Aromatics	ASTM—D1319
Freeze Point	ASTM—D2386
Reid Vapor Pressure	ASTM—D323
Flash Point	ASTM—D56
Distillation	ASTM—D86
Heat of Combustion	ASTM—D3338

1. In Situ Crude Shale Oil. Samples of crude in situ shale oil were processed into JP-4 and JP-8 turbine fuel samples. In each case, at least 100 hours on stream were provided in the crude shale oil hydrotreater, and the remainder of the process modules operated as necessary to exhaust the available samples.

SAMPLE M-112

The crude shale oil hydrotreating step for sample M-112 was provided as run M-11. Sample M-112 was prepared from the composite product by fractionation to a nominal 600°F (atmospheric) cut point, producing an IBP to 600°F distillate and a 600°F+ gas oil for FCC charge.

The raw in situ oil was processed for five days over cobalt molybdate catalyst. Details of this study are available in Volume II of this report. In general, the run was reasonably stable during the 100+ hours of operation although apparent catalyst equilibration did not occur until after about 70 hours of operation. Table V-3 presents the overall normalized yield structure based on feed for the 600°F fractionation.

Fluid cracking of the 600°F+ M-112 sample was smooth with reasonably good recovery, although high carbon-on-regenerated-catalyst levels and high catalyst-to-oil ratios were encountered. The poor regeneration provided can be expected to depress distillate yields obtainable, while the high catalyst circulation rate, as well as the high residual

TABLE V-3

M-112 YIELD STRUCTURE

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.40	-	0.02	-	0.09	-	-	-
NH_3	0.47	-	0.50	-	0.30	-	-	-
H_2O	0.86	-	0.20	-	0.18	-	-	-
H_2	-1.29	0.22	-0.50	-	-0.87	1.42	-1.32	-
C_1	-	0.72	-	-	0.19	0.38	-	-
C_2	0.09	1.96	0.03	-	0.35	0.54	-	-
C_3	0.08	0.87	0.04	-	0.68	1.03	-	-
$C_3=$	-	2.15	-	-	-	-	-	-
C_4	0.29	0.90	0.03	-	0.71	0.87	-	-
$C_4=$	-	2.78	-	-	-	-	-	-
C_5	0.01	-	0.04	-	0.56	0.39	-	-
C_5+ Losses	-	3.09	-	-	0.61	0.90	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	37.22	31.82	-	92.48	97.20	94.47	101.32	-
Separated Diesel	-	-	-	-	-	-	-	-
600+	61.87	43.10	99.64	-	-	-	-	-
Coke	-	12.39	-	-	-	-	-	-
Extract	-	-	-	7.52	-	-	-	-
Feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	-

carbon levels, lead to higher than expected coke yields. Due to mechanical limitations of the unit, a relatively high (~10 percent of total distillate) loss of nominal C_5 to C_6 components was encountered. Of particular interest, nominal levels of 33 percent denitrogenation and 41 percent desulfurization were also obtained during cracking. The total recovered FCC product was fractionated again to a 600°F cut point, with the bottoms product diverted to recycle hydrotreater studies.

The cracked distillate (IBP to 600°F) product was blended quantitatively with the hydrotreater distillate product and provided to the extraction unit. Basic nitrogen removal of 93.6 percent was attained, with roughly 92.5 percent of the distillate charge recovered as reduced nitrogen content raffinate. The raffinate was water washed and provided to the guardcase operation.

The initial guardcase operation on this sample was not successful in reducing sulfur and nitrogen contaminants to <1 ppm each. Postulated at that time, and later verified, was that incomplete cleanup from the extraction operation had resulted in catalyst poisoning. As a result, the material was rehydrotreated successfully to <1 ppm sulfur and nitrogen. The requirement of two hydrotreating and product handling steps at this point resulted in higher hydrogen consumption, gas make and product handling loss, with a resulting lower liquid yield than would otherwise have been observed. In order to track freeze point and aromatic content of the (targeted) JP-4 fraction through further processing, a component fractionation was performed on the initial hydrotreating product, with the results shown in Table V-4. Yields were 74.2 weight percent JP-4 fraction, 24.9 weight percent diesel fraction, plus a 0.9 weight percent overall loss on a batch Todd distillation. Light end losses were apparent, as indicated by the measured 0.85 RVP of the JP-4 fraction.

This nominal I to 520°F JP-4 fraction was fed to freeze point modification, resulting in a 23°F freeze point depression, 1.42 weight percent hydrogen yield and a 94.5 weight percent liquid yield. Nine-tenths weight percent of feed was lost as C_5+ components in the gas stream.

The entire reformer product was processed through aromatic saturation to reduce the 40 percent aromatic content to less than 25 percent. A normalized 101.32 weight percent yield of product was obtained at an aromatics content of 18.3 volume percent.

Overall, observed yields (normalized) are shown in Table V-4 based on a crude shale oil feed of 100 pounds. Actual yield of JP-4, as observed, was 42 volume percent of feed.

Table V-5 demonstrates calculated no-loss yields for this sample when recycle is practiced. A JP-4 yield of at least 54 volume percent could be expected. Vapor pressure of the sample, based on addition of the light ends losses,

TABLE V-4

M-112 ACTUAL YIELDS

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.40	-	0.01	-	0.05	-	-	0.46
NH_3	0.47	-	0.13	-	0.16	-	-	0.76
H_2O	0.86	-	0.05	-	0.09	-	-	1.00
H_2	-1.29	0.14	-0.13	-	-0.46	0.54	-0.47	-1.67
C_1	0.00	0.45	0.00	-	0.10	0.14	-	0.69
C_2	0.09	1.21	0.01	-	0.18	0.21	-	1.70
C_3	0.08	0.54	0.01	-	0.36	0.39	-	1.38
C_3=	0.00	1.33	0.00	-	0.00	-	-	1.33
C_4	0.29	0.56	0.01	-	0.37	0.33	-	1.56
C_4=	0.00	1.72	0.00	-	0.00	-	-	1.72
C_5	0.01	0.00	0.01	-	0.29	0.15	-	0.46
C_5+ Losses	0.00	1.91	0.00	-	0.79	0.34	-	3.04
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	37.22	19.69	-	52.62	37.98	35.88	36.35	36.35
Separated Diesel	-	-	-	-	12.71	-	-	12.71
600+	61.87	26.66	26.56	-	-	-	-	26.56
Coke	-	7.67	-	-	-	-	-	7.67
Extract	-	-	-	4.28	-	-	-	4.28
Feed	100	61.87	26.66	56.90	-	52.62	37.98	35.88

TABLE V-5

M-112 NO-LOSS YIELDS WITH RECYCLE

	CSHT	* FCC	* COHT	EXT	GC	REF	AR SAT	TO- TAL
H_2S	0.40	-	0.01	-	0.06	-	-	0.47
NH_3	0.47	-	0.16	-	0.20	-	-	0.83
H_2O	0.86	-	0.06	-	0.12	-	-	1.04
H_2	-1.29	0.26	-0.16	-	-0.58	0.69	-0.61	-1.69
C_1	-	0.87	0.00	-	0.13	0.19	-	1.19
C_2	0.09	1.71	0.01	-	0.23	0.26	-	2.30
C_3	0.08	1.05	0.01	-	0.45	0.50	-	2.09
$C_3=$	-	2.52	0.00	-	0.00	-	-	2.52
C_4	0.29	2.24	0.01	-	0.47	0.42	-	3.43
$C_4=$	-	2.81	0.00	-	0.00	-	-	2.81
C_5	0.01	1.56	0.01	-	0.37	0.19	-	2.14
C_5+ Losses	-	-	-	-	-	-	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	37.22	34.55	-	66.37	48.79	46.54	47.15	47.15
Separated Diesel	-	-	-	-	16.13	-	-	16.13
600+	61.87	4.85	4.74	-	-	-	-	4.74
Coke	-	9.45	-	-	-	-	-	9.45
Extract	-	-	-	5.40	-	-	-	5.40
Feed	100.00	88.44	31.51	71.77	66.37	48.79	46.54	100.00

* - NET YIELDS ONLY

would easily be within the 2 to 3 RVP specification ranges. These data are presented schematically in Figure V-1.

The most impressive factor in this sample preparation, as shown in Table V-6, is the potential for a high hydrogen content (14.6 weight percent) JP-4 stream, at over 50 volume percent of crude shale oil charge, while requiring only 1020 standard cubic feet of chemical hydrogen consumption per barrel of crude shale oil charge.

SAMPLE M-121

The crude shale oil hydrotreating requirement for sample M-121 was provided identically to that practiced for sample M-112, except that nickel molybdate catalyst was used instead of cobalt molybdate. Fractionation was again performed to a 600°F atmospheric cut point, with the nominal 600°F+ bottoms fed to the FCC unit. Again, hydrotreater operation was reasonably smooth, but with apparent catalyst equilibration again requiring roughly 70 hours of operation.

Summary yield structures for the entire process are shown in Table V-7. All operations are analogous to those performed for sample M-112. Residual carbon-on-catalyst for the FCC operation on this sample was, however, reduced to acceptable levels. Very high catalyst circulation rates and light ends losses were again encountered.

Comparable problems were also encountered in the guard-case operations, requiring two hydrotreating steps to be performed with the concomitant high hydrogen consumption,

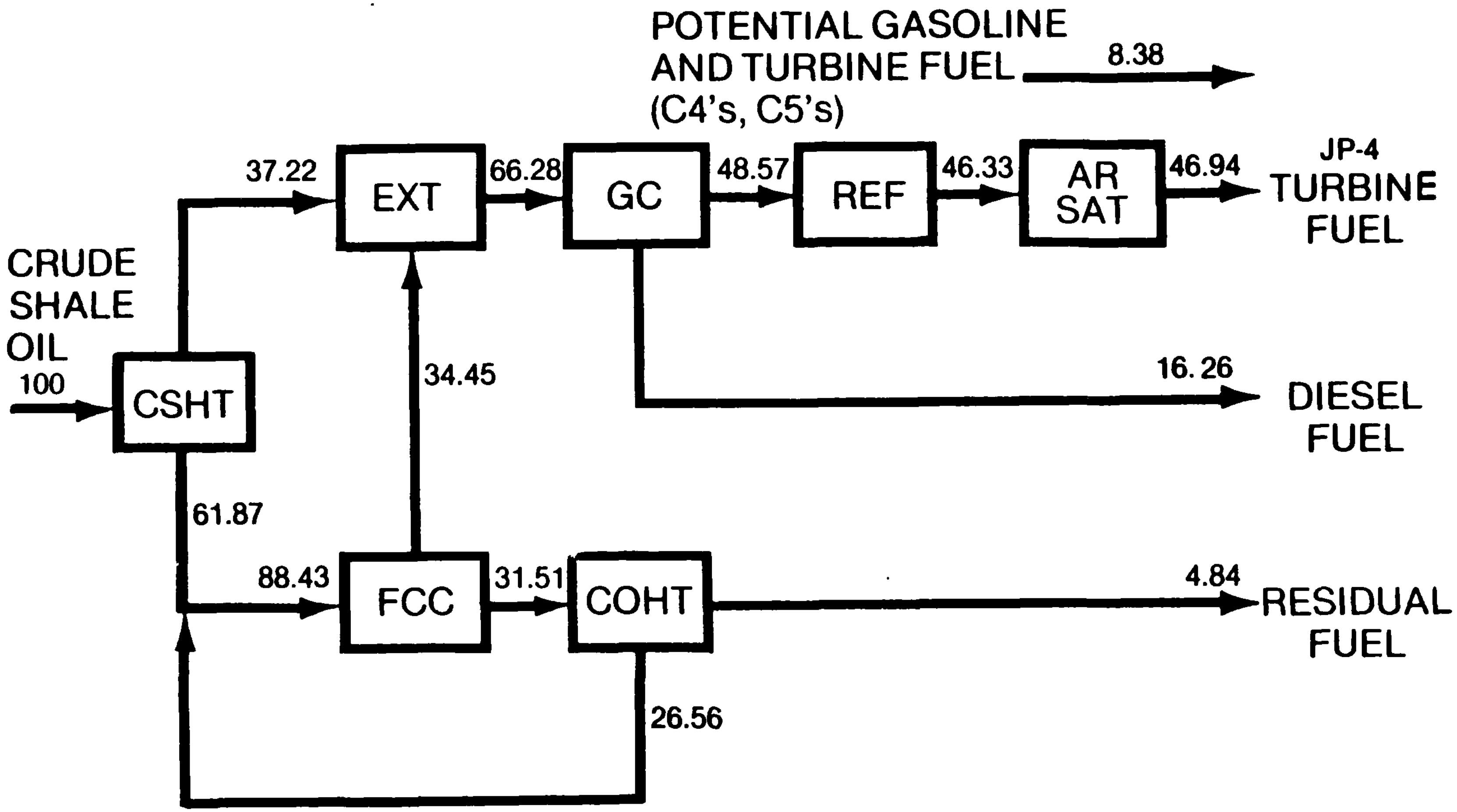


Figure V-1. Sample M-112 – Target: JP-4

TABLE V–6

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No.	M-112	
Fuel Type	JP-4	
Shale Source	In Situ	Specifications
Gravity, API	46.7	45-57
Hydrogen, Wt%	14.6	13.6 min
Saturates, Vol%	80.9	
Olefins, Vol%	0.8	
Aromatics, Vol%	18.3	25.0 max
Freeze Point, °F	—81	—72 max
RVP, PSI		2-3
Flash Point, °F		
Heat of Combustion, BTU/#	18,584	18,400 min
Distillation, °F		
IBF	218	
10%	226	
20%	314	
50%	379	
90%	454	
FBP	490	
Residue	1.0	
Loss	1.0	

TABLE V-7

M-121 YIELD STRUCTURE

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TOTAL
H_2S	0.43	-	0.02	-	0.07	-	-	-
NH_3	0.51	-	0.57	-	0.27	-	-	-
H_2O	0.82	-	0.25	-	0.17	-	-	-
H_2	-0.88	0.15	-0.50	-	-1.59	1.15	-1.89	-
C_1	-	-	0.10	-	0.20	0.38	-	-
C_2	0.09	1.60	0.00	-	0.36	0.57	-	-
C_3	0.08	0.64	0.10	-	0.85	1.09	-	-
$C_3=$	-	2.81	-	-	0.00	-	-	-
C_4	0.07	1.04	0.15	-	0.36	0.90	-	-
$C_4=$	-	4.01	-	-	0.00	-	-	-
C_5	0.09	-	0.04	-	0.36	0.54	-	-
C_5+ Losses	-	3.71	-	-	0.65	0.61	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	32.66	35.30	-	90.08	98.30	94.76	101.89	-
Separated Diesel	-	-	-	-	-	-	-	-
600+	66.13	35.64	99.27	-	-	-	-	-
Coke	-	15.10	-	-	-	-	-	-
Extract	-	-	-	9.92	-	-	-	-
Feed	100.00	100.00	100.00	100.00	100.00	100 00	100.00	100.00

gas production and liquid losses. Since this sample was targeted for JP-8 production, the entire IBP to 600°F sample was charged to the reforming operation. The inherent gasoline fraction was separated after reforming and the nominal 310 to 600°F fraction charged to aromatic saturation.

Table V-8 presents an overall yield structure for the M-121 sample. A slightly higher overall hydrogen consumption was encountered than for M-112, primarily due to higher hydrogen requirements in the guardcase and aromatic saturation sections. A slightly higher (by one weight percent) turbine fuel yield was attained for M-121. However, total distillate liquid yield was slightly higher (again by about one percent) for the M-112 sample. Actual JP-8 yield was 43 volume percent of crude shale oil prior to final sample blending.

The product from aromatic saturation did not meet freeze point specifications, even though a 12°F freeze point depression had been attained during reforming. This was primarily due to a high quantity of 500°F+ material in the sample. This sample was then fractionated to remove heavy materials. Removal of 12.6 volume percent of heavy material produced a specification JP-8. This reduced the actual specification JP-8 yield to 36 volume percent of crude shale oil charge.

Table V-9 and Figure V-2 present calculated, no-loss yields for this sample when practicing recycle to the FCC unit. The aforementioned final distillation correction has

TABLE V-8

M-121 ACTUAL YIELDS

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.43	-	-	-	0.04	-	-	0.47
NH_3	0.51	-	0.13	-	0.14	-	-	0.78
H_2O	0.82	-	0.06	-	0 09	-	-	0.97
H_2	-0.88	0.10	-0.12	-	-0.80	0.57	-0.70	-1.83
C_1	-	-	0.02	-	0.10	0.19	-	0.31
C_2	0.09	1.06	0.00	-	0.18	0.28	-	1.61
C_3	0.08	0.42	0.02	-	0.43	0.54	-	1.49
$C_3=$	-	0.86	0.00	-	0.00	-	-	1.86
C_4	0.07	0.69	0.04	-	0.18	0.45	-	1.43
$C_4=$	-	2.65	0.00	-	0.00	-	-	2.65
C_5	0.09	-	0.01	-	0.18	0.27	-	0.55
C_5+ Losses	-	2.45	0.00	-	0.33	0.37	-	3.15
Separated Gasoline	-	-	-	-	-	10.01	-	10.01
C_6-600 or Heartcut	32.66	23.34	-	50.44	49.57	36.89	37.59	37.59
Separated Diesel	-	-	-	-	-	-	-	-
600+	66.13	23.57	23.41	-	-	-	-	23.41
Coke	-	9.99	-	-	-	-	-	9.99
Extract	-	-	-	5.56	-	-	-	5.56
Feed	100 00	66.13	23.57	56.00	50.44	49.57	36.89	100.00

TABLE V-9

M-121 NO-LOSS YIELDS WITH RECYCLE

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO- TAL
H_2S	0.43	-	-	-	0.04	-	-	0.47
NH_3	0.51	-	0.15	-	0.17	-	-	0.83
H_2O	0.82	-	0.07	-	0.11	-	-	1.00
H_2	-0.88	0.21	0.21	-	-1.00	0.64	-0.76	-1.93
C_1	-	0.37	0.02	-	0.13	0.21	-	0.73
C_2	0.09	1.50	-	-	0.23	0.32	-	2.14
C_3	0.08	0.87	0.02	-	0.53	0.61	-	2.11
C_3=	-	2.91	-	-	-	-	-	2.91
C_4	0.07	2.17	0.05	-	0.23	0.50	-	3.02
C_4=	-	3.61	-	-	-	-	-	3.61
C_5	0.09	1.37	0.01	-	0.23	0.30	-	2.00
C_5+ Losses	-	-	-	-	-	-	-	-
Separated Gasoline	-	-	-	-	-	12.63	-	12.63
C_6-600 or Heartcut	32.66	37.12	-	62.86	55.53	40.32	41.08	41.08
Separated Diesel	-	-	-	-	6.66	-	-	6.66
600+	66.13	4.28	4.26	-	-	-	-	4.26
Coke	-	11.56	-	-	-	-	-	11.56
Extract	-	-	-	6.92	-	-	-	6.92
Feed	100.00	89.54	27.85	69.78	62.86	55.53	40.32	100.00

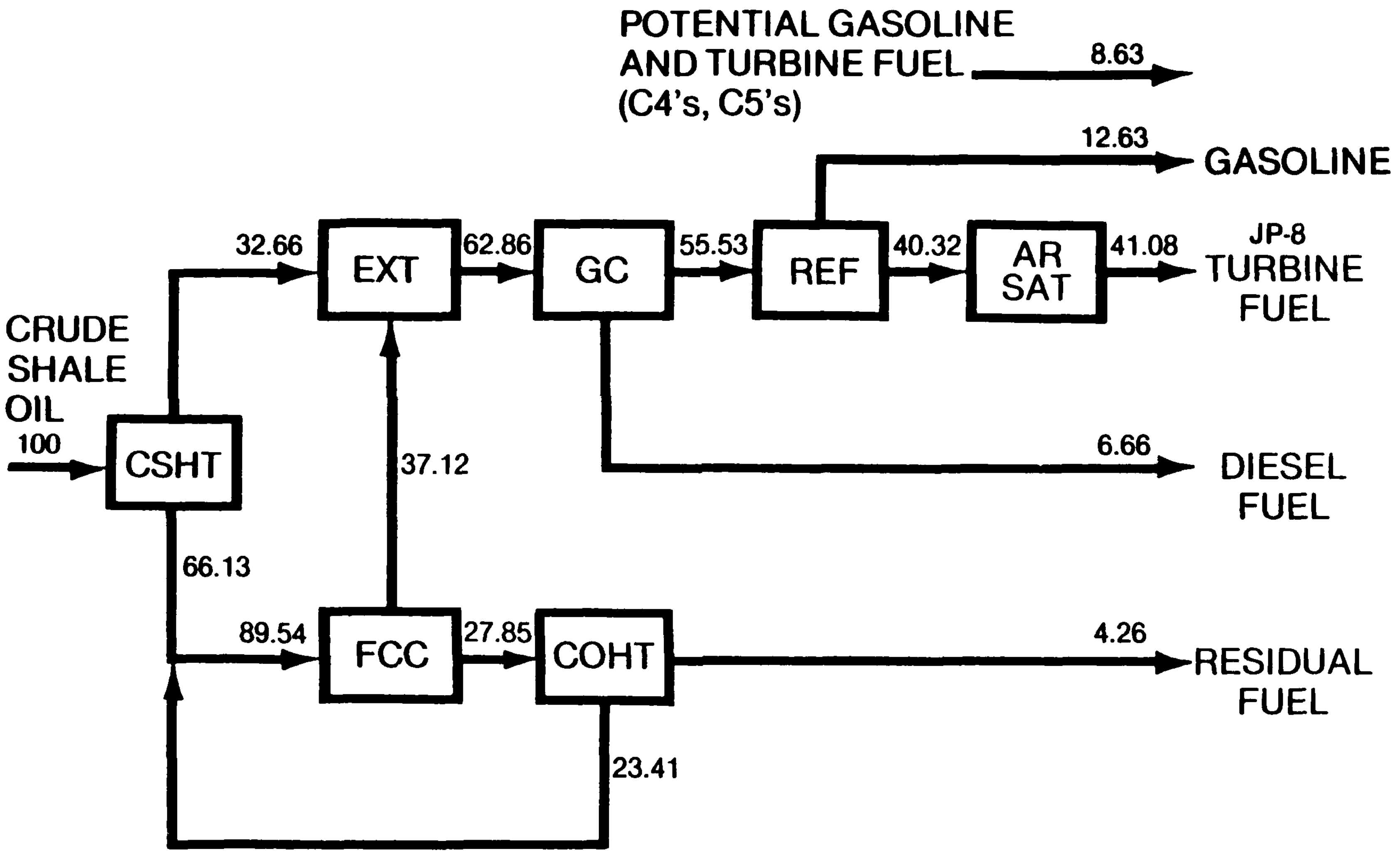


Figure V-2. Sample M-121 - Target JP-8

been provided more properly after the guardcase rather than after total processing. A net 1160 SCFB of hydrogen was required based on shale oil feed, producing roughly 47 volume percent of crude shale oil feed as JP-8 fuel.

Table V-10 presents sample properties for the JP-8 turbine fuel produced.

SAMPLE GC-1

Sample GC-1 was provided as the best simulation possible of expected actual plant practice. The production method was by concurrent preparation of all pertinent military fuel samples, plus the use of aging test products to simulate true steady state and/or average catalyst age products. Further, this sample was also designed to test feeding full range hydrotreater product to the FCC unit.

The crude shale oil was hydrotreated over cobalt molybdate catalyst at estimated optimum conditions for a nominal period of 30 days. Product composites covering the entire run were stabilized and fed to the FCC unit without fractionation.

The FCC distillate was extracted as before, and the extraction raffinate provided to the guardcase. During this sequence, however, a new, specially designed raffinate cleanup system was used to provide a non-contaminated feed to the guardcase.

TABLE V-10

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No. Fuel Type Shale Source	M-121 JP-8 In Situ	Specifications
Gravity, API	41.4	37-51
Hydrogen, Wt%	13.8	13.6 min
Saturates, Vol%	78.6	
Olefins, Vol%	1.0	
Aromatics, Vol%	20.4	25.0 max
Freeze Point, °F	—64	—58 max
RVP, PSI		
Flash Point, °F	132	100 min
Heat of Combustion, BTU/#	18,542	18,400 min
Distillation, °F		
IBP	340	
10%	373	
20%	387	
50%	422	
90%	475	
FBP	498	
Residue	1.0	
Loss	1.0	

The guardcase operation was performed by incrementally increasing severity to define actual minimum severity required to produce <1 ppm sulfur and nitrogen product. Due to slow analytical turnaround, however, and expectations based on previous (contaminated) sample requirements, required conditions were attained almost at once and overshot by a significant margin. When this fact was discovered, conditions were frozen and the run continued to the end of feed (~4 days). No aging was noted, as might be expected due to the higher than required conditions used. At this point, the best estimate available for removal of diesel fractions was used. Four and one-half weight percent of the guardcase product was removed as 580°F+ nominal bottoms.

This -580°F distillate was processed through the reformer under accelerated aging conditions of approximately two months of commercial operation. The entire product was composited, stabilized, and aromatic saturated to a very low level of total aromatics.

This composite sample was then fractionated into pseudocomponents, and pertinent fuel samples prepared by blending.

Table V-11 shows yield structures encountered during these studies, and Table V-12 actual overall process yields. While the overall process yield structure is biased negatively by the excessive severity in the guardcase and reformer (due to other objectives), the conversion module is appropriate for comparison to M-112 and M-121. For this

TABLE V-11

GC-1 YIELD STRUCTURE

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.52	-	-	-	0.07	-	-	-
NH_3	0.31	-	-	-	0.23	-	-	-
H_2O	0.84	-	-	-	0.16	-	-	-
H_2	-1.21	0.19	-	-	-1.26	-1.26	-1.20	-
C_1	0.12	0.59	-	-	0.11	1.14	-	-
C_2	0.33	1.07	-	-	0.45	1.95	-	-
C_3	0.26	0.47	-	-	1.14	1.44	0.18	-
C_3=	-	1.71	-	-	-	-	-	-
C_4	0.31	0.73	-	-	0.46	1.69	0.54	-
C_4=	-	2.16	-	-	-	-	-	-
C_5	0.02	-	-	-	0.76	0.90	1.00	-
C_5+ Losses	-	1.31	-	-	3.68	0.10	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	98.50	48.06	-	95.17	91.20	91.52	99.48	-
Separated Diesel	-	-	-	-	-	-	-	-
600+	-	31.49	-	-	-	-	-	-
Coke	-	12.22	-	-	-	-	-	-
Extract	-	-	-	4.83	-	-	-	-
Feed	100.00	100.00	-	100.00	100.00	100.00	100.00	100.00

AD-A127 329 REFINING OF MILITARY JET FUELS FROM SHALE OIL VOLUME I 3/3
PART II PREPARATIO..(U) ASHLAND PETROLEUM CO KY
H F MOORE MAR 82 AFWAL-TR-81-2056-VOL-1-PT-2
UNCLASSIFIED F33615-78-C-2080 F/G 21/4 NL

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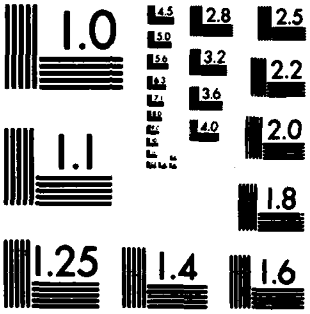

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE V-12

GC-1 ACTUAL YIELDS

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.52	-	-	-	0.03	-	-	-
NH_3	0.31	-	-	-	0.10	-	-	-
H_2O	0.84	-	-	-	0.07	-	-	-
H_2	-1.21	0.19	-	-	-0.57	0.51	-0.45	-
C_1	0.12	0.58	-	-	0.05	0.46	-	-
C_2	0.33	1.05	-	-	0.20	0.79	-	-
C_3	0.26	0.46	-	-	0.51	0.58	0.07	-
$C_3^=$	-	1.68	-	-	-	-	-	-
C_4	0.31	0.72	-	-	0.21	0.68	0.20	-
$C_4^=$	-	2.13	-	-	-	-	-	-
C_5	0.02	-	-	-	0.34	0.36	0.37	-
C_5+ Losses	-	1.29	-	-	1.66	0.04	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	98.50	47.34	-	45.05	40.53	37.11	36.92	-
Separated Diesel	-	-	-	-	1.91	-	-	-
600+	-	31.02	-	-	-	-	-	-
Coke	-	12.04	-	-	-	-	-	-
Extract	-	-	-	2.29	-	-	-	-
Feed	100.00	98.50	-	47.34	45.05	40.53	37.11	-

sample, distillate (I to 600°F) and, in particular, light distillate (I to 400°F) yields from the FCC were obviously suppressed by inclusion of distillate material in the feed. Extract yield and total nitrogen content of the extraction module feed were, however, reduced.

Final properties of the combined C_6 to 600°F distillate were such that only low volumes of turbine fuel could be blended. With more time and care, additional turbine fuel could have been blended.

Finally, total hydrogen consumption was only 920 SCFB of crude shale oil charge. Recycle of bottoms product, not practiced due to time and equipment limitations, would have proportionately increased both yields and hydrogen consumption on a relative basis comparable to the M-112 and M-121. An example flow diagram for this sample, if recycle were practiced, is shown in Figure V-3. JP-4 and JP-8 fuel properties are shown in Tables V-13 and V-14.

CONCLUSIONS

Based on these data, and these data only, the following conclusions can be drawn:

- Front-end hydrotreating over cobalt molybdate catalyst and feeding fractionated material to the FCC unit is favored on the basis of both distillate yield and potential distillate yield (distillate + recycle).
- Product quality considerations lead to analogous conclusions as above.

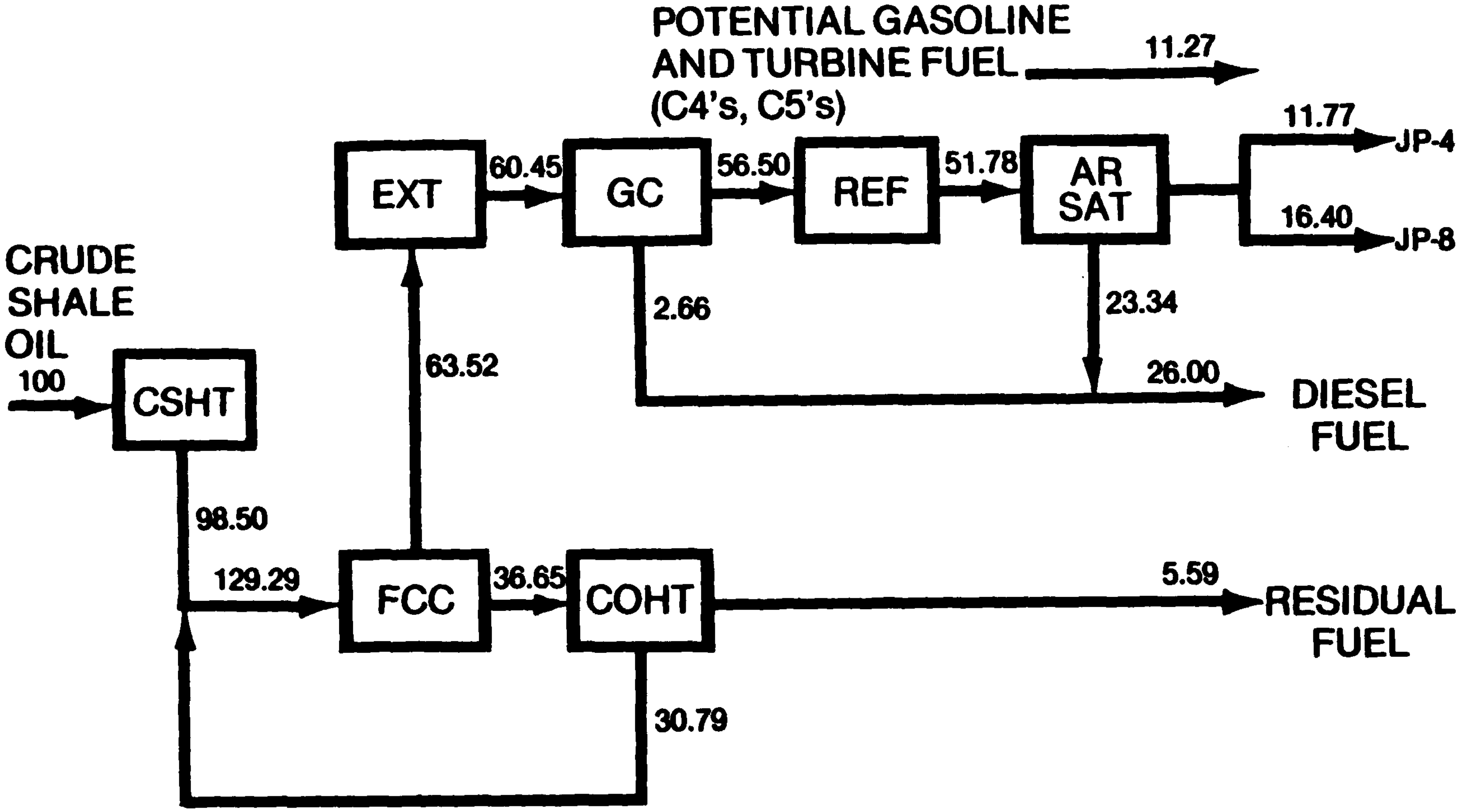

Figure V-3. Sample GC-1 - Concurrent Fuel Production

TABLE V-13

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No.	GC1-4	
Fuel Type	JP-4	
Shale Source	In Situ	Specifications
Gravity, API	52.6	45-57
Hydrogen, WT%	14.6	13.6 min
Saturates, Vol%	94.5	
Olefins, Vol%	0.7	
Aromatics, Vol%	4.8	25.0 max
Freeze Point, °F	—90	—72 max
RVP, PSI	1.5	2-3
Flash Point, °F		
Heat of Combustion, BTU/#	18,769	18,400 min
Distillation, °F		
IBF	156	
10%	228	
20%	253	
50%	304	
90%	387	
FBP	412	
Residue	1.0	
Loss	1.0	

TABLE V-14

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No.	GC 1-8	
Fuel Type	JP-8	
Shale Source	In Situ	Specifications
Gravity, API	44.8	37-51
Hydrogen, Wt%	14.1	13.6 min
Saturates, Vol%	88.9	
Olefins, Vol%	0.8	
Aromatics, Vol%	10.3	25.0 max
Freeze Point, °F	—64	—58 max
RVP, PSI		
Flash Point, °F	96	100 min
Heat of Combustion, BTU/#	18,637	18,400 min
Distillation, °F		
IBP	286	
10%	321	
20%	336	
50%	373	
90%	458	
FBP	506	
Residue	1.0	
Loss	0.5	

- While the nickel molybdate hydrotreater sample (M-121) might provide analogous yield potential at similar hydrogen consumptions, the requirement for higher severity, leading to higher denitrogenation, results in the cobalt molybdate case still being favored.
- In particular, feeding a full range liquid <u>in this case</u> appears to markedly suppress light distillate production while increasing the less desirable fuel gas production reactions.

2. <u>Above-Ground Crude Shale Oil</u>. Samples of crude above-ground shale oil were processed into JP-4, JP-5, JP-8, and broad-range (expanded specification) turbine fuels. In each case, samples were based on at least 100 hours on-stream in the crude shale hydrotreater, with the remaining process modules operated as necessary to exhaust the available sample.

SAMPLE M-212

The crude shale oil hydrotreating step for sample M-212 was provided as run M-21. Sample M-212 was prepared from the composite product by fractionation to a nominal 600°F (atmospheric) cut point, producing an IBP to 600°F distillate and a 600°F+ gas oil for FCC charge. Table V-15 presents module yields.

TABLE V-15

M-212 YIELD STRUCTURE

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.45	-	0.26	-	0.20	-	-	-
NH_3	0.35	-	1.49	-	0.46	-	-	-
H_2O	0.80	-	0.21	-	-	-	-	-
H_2	-2.40	0.25	-0.84	-	-2.07	1.08	-0.62	-
C_1	0.02	0.89	0.20	-	0.15	0.83	-	-
C_2	0.54	1.93	0.10	-	0.41	0.65	0.02	-
C_3	0.48	0.79	0.10	-	0.72	1.13	0.06	-
C_3=	-	2.10	-	-	-	-	-	-
C_4	0.46	0.75	0.12	-	0.59	0.83	0.25	-
C_4=	-	2.53	-	-	-	-	-	-
C_5	0.28	-	0.07	-	0.43	0.41	0.46	-
C_5+ Losses	-	1.58	-	-	4.45	-	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	30.52	27.22	-	89.05	94.66	95.07	99.83	-
Separated Diesel	-	-	-	-	-	-	-	-
600+	68.50	48.08	98.29	-	-	-	-	-
Coke	-	13.88	-	-	-	-	-	-
Extract	-	-	-	10.95	-	-	-	-
Feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	-

The raw above-ground oil was processed for 5 days over cobalt molybdate catalyst. Details of this study are available in Volume III of this report. In general, the run was reasonably stable during the 100+ hours of operation although apparent catalyst equilibration did not occur until after about 70 hours of operation.

Table V-16 shows the actual yield balance for the entire EXTRACTACRACKING module results from Phase II for this sample.

Fluid cracking of the 600°F+ M-212 sample was smooth with reasonably good recovery, although high carbon-on-regenerated-catalyst levels and high catalyst-to-oil ratios were encountered. The poor regeneration provided can be expected to depress distillate yields obtainable, while the high catalyst circulation rate, as well as the high residual carbon levels, led to higher-than-expected coke yields. Of particular interest, good apparent denitrogenation and desulfurization levels were obtained during cracking, along with an excellent hydrogen partition. The total recovered FCC product was fractionated again to a 600°F cut point, with the bottoms product diverted to recycle hydrotreater studies.

For the purpose of examining in detail the impact of catalytically cracked products on the extraction module, the hydrotreated and catalytically cracked M-212 distillates were processed separately through both extraction and initial guardcase sequences. Problems with contamination of the

·TABLE V-16

M-212 ACTUAL YIELDS

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.45	-	0.09	-	0.09	-	-	0.63
NH_3	0.35	-	0.49	-	0.20	-	-	1.04
H_2O	0.80	-	0.07	-	-	-	-	0.87
H_2	-2.40	0.17	-0.28	-	-0.91	0.44	-0.24	-3.22
C_1	0.02	0.61	0.07	-	0.07	0.34	0.00	1.11
C_2	0.54	1.32	0.03	-	0.18	0.27	0.01	2.35
C_3	0.48	0.54	0.03	-	0.32	0.47	0.02	1.86
C_3=	-	1.44	-	-	-	-	-	1.44
C_4	0.46	0.51	0.04	-	0.26	0.34	0.10	1.71
C_4=	-	1.73	-	-	-	-	-	1.73
C_5	0.28	-	0.02	-	0.19	0.17	0.18	0.84
C_5+ Losses	-	1.08	-	-	1.95	-	-	3.03
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	30.52	18.65	-	43.79	41.44	39.41	39.34	39.34
Separated Diesel	-	-	-	-	-	-	-	-
600+	68.50	32.94	32.38	-	-	-	-	32.38
Coke	-	9.51	-	-	-	-	-	9.51
Extract	-	-	-	5.38	-	-	-	5.38
Feed	100.00	68.50	32.94	49.17	43.79	41.44	39.41	100.00

guardcase charge were again encountered, requiring rehydrotreatment of the initial guardcase product. This rehydrotreatment was accomplished in a single step, by combining both streams. An IBP to 520°F fraction was fed to the reforming section where a +20 percent aromatics change resulted in a freeze point reduction of about 23°F. Final saturation of those aromatics to 24 percent resulted in a freeze point of -64°F.

Loss of light ends during processing prevented final submission of this sample as a JP-4 grade fuel. In addition, the high preponderence of +300°F material (TBP basis) resulted in a skewed distillation range for the sample, directly leading to the unacceptable -64°F freeze point. Further evaluation of this sample demonstrated its intermediate status between JP-4 and JP-8. Since the number of required samples had already been satisfied by other materials, this sample was provided as an additional increment representing a potential broad-range (expanded specification) fuel. Properties of this sample are shown in Table V-17.

An overall yield structure for this sample, on a no-loss basis, is presented in Table V-18 and Figure V-4 when practicing FCC recycle. An excellent 55.2 weight percent heartcut could be obtained at the conditions used, representing a 63.9 volume percent potential broad-range turbine fuel yield based on crude shale oil charge. A relatively high hydrogen consumption of 2000 SCFB was encountered in this sample, directly attributable to the high consumption

TABLE V–17

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No.	M-212
Fuel Type	Broad Range
Shale Source	Above Ground
Gravity, API	44.6
Hydrogen, Wt%	14.0
Saturates, Vol%	74.7
Olefins, Vol%	1.0
Aromatics, Vol%	24.3
Freeze Point, °F	—64
RVP, PSI	
Flash Point, °F	
Heat of Combustion, BTU/#	18,546
Distillation, °F	
IBP	241
10%	309
20%	336
50%	398
90%	466
FBP	500
Residue	1.0
Loss	1.0

TABLE V-18

M-212 NO-LOSS YIELDS WITH RECYCLE

* Net Yields

	CSHT	* FCC	* COHT	* EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.45	-	0.10	-	0.12	-	-	0.67
NH_3	0.35	-	0.57	-	0.27	-	-	1.19
H_2O	0.80	-	0.08	-	-	-	-	0.88
H_2	-2.40	0.38	-0.32	-	-1.21	0.63	-0.34	-3.26
C_1	0.02	1.74	0.08	-	0.09	0.48	-	2.41
C_2	0.54	3.06	0.04	-	0.24	0.38	0.01	4.27
C_3	0.48	1.31	0.04	-	0.42	0.66	0.03	2.94
$C_3=$	-	3.09	-	-	-	-	-	3.09
C_4	0.46	1.53	0.05	-	0.35	0.48	0.14	3.01
$C_4=$	-	3.17	-	-	-	-	-	3.17
C_5	0.28	0.79	0.03	-	0.25	0.24	0.25	1.84
C_5+ Losses	-	-	-	-	-	-	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	30.52	35.39	-	58.69	58.16	55.29	55.20	55.20
Separated Diesel	-	-	-	-	-	-	-	-
600+	68.50	5.14	5.05	-	-	-	-	5.05
Coke	-	12.32	-	-	-	-	-	12.32
Extract	-	-	-	7.22	-	-	-	7.22
Feed (Gross)	100.00	101.88	38.10	65.91	58.69	58.16	55.29	100.00

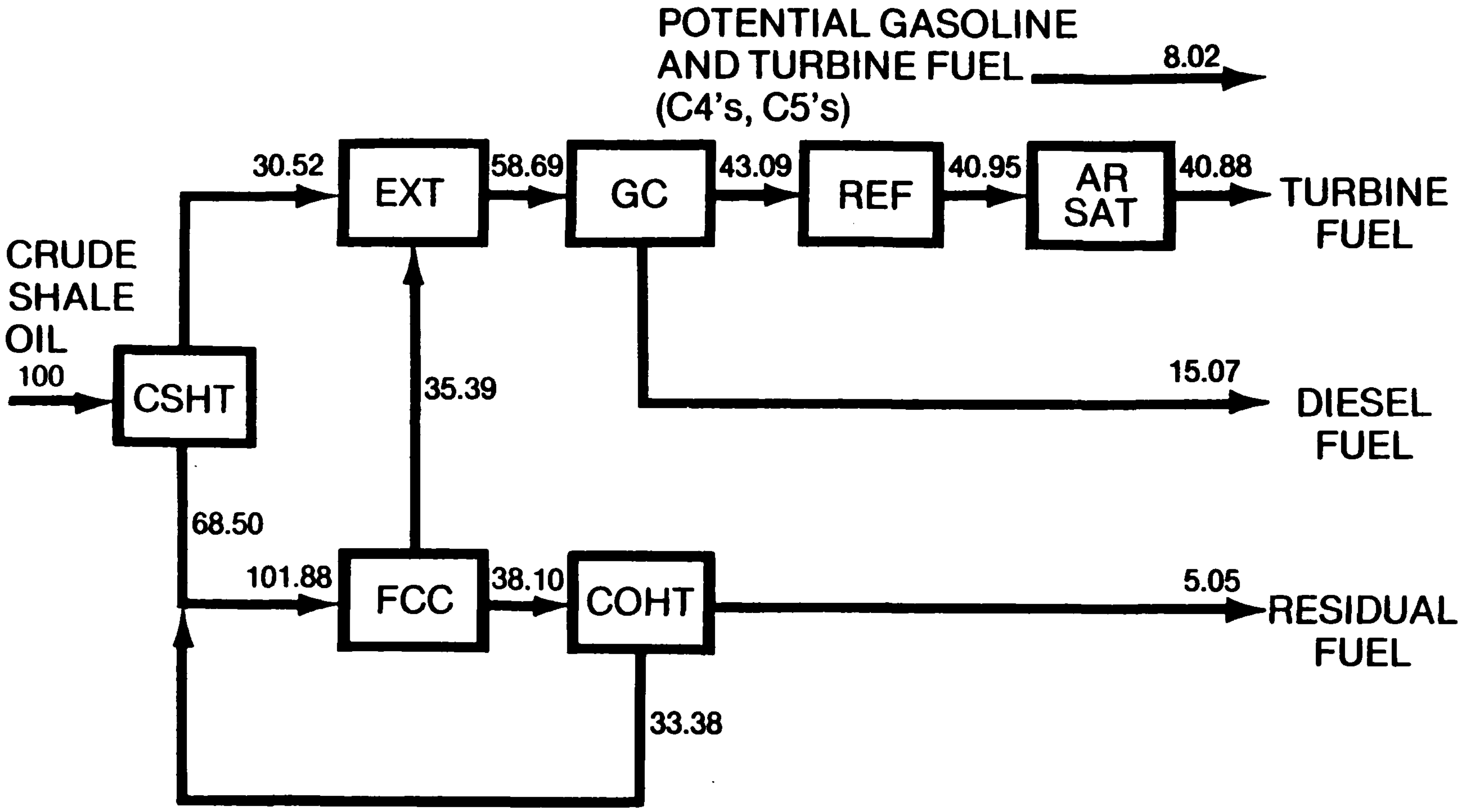

Figure V-4. Sample M-212 - Target: Broad-range Turbine Fuel

(~1500 SCFB) encountered in the crude shale oil hydrotreater. This consumption level is excessive and would not normally be encountered at these conditions. Excessive gas production was encountered in the crude shale hydrotreater, guardcase, reformer and aromatic saturation unit, contributing not only to high hydrogen consumption, but also to lowered liquid yields.

The processing results for sample M-212 demonstrate that optimum conditions were not provided for this sample. A very large potential for improvement is apparent.

SAMPLE M-221

The crude shale oil hydrotreating requirement for sample M-221 was provided identically to that practiced for sample M-212, except that nickel molybdate catalyst was used instead of cobalt molybdate. Fractionation was again performed to a 600°F atmospheric cut point, with the nominal 600°F+ bottoms fed to the FCC unit. Again, hydrotreater operation was reasonably smooth, but with apparent catalyst equilibration again requiring roughly 70 hours of operation.

Summary yield structures for the entire process are shown in Table V-19. All operations are analogous to those performed for sample M-212. Residual carbon-on-catalyst for the FCC operation on this sample was, however, reduced to acceptable levels. Very high catalyst circulation rates and light ends losses were again encountered.

TABLE V-19

M-221 YIELD STRUCTURE

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.49	-	0.22	-	0.19	-	-	-
NH_3	0.24	-	0.92	-	0.40	-	-	-
H_2O	0.79	-	0.45	-	-	-	-	-
H_2	-1.52	0.22	-1.14	-	-1.12	1.54	-1.14	-
C_1	-	0.88	0.09	-	0.00	0.70	0.25	-
C_2	0.73	1.96	0.72	-	0.36	0.58	-	-
C_3	0.65	0.70	0.68	-	0.74	1.10	0.12	-
C_3=	-	2.22	-	-	-	-	-	-
C_4	0.50	0.71	0.39	-	0.62	0.66	0.79	-
C_4=	-	2 66	-	-	-	-	-	-
C_5	0.89	-	0.23	-	0.71	0.35	1.19	-
C_5+ Losses	-	2.62	-	-	4.27	-	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	25.61	31.04	-	90.19	93.83	95.07	98.79	-
Separated Diesel	-	-	-	-	-	-	-	-
600+	71.62	37.38	97.74	-	-	-	-	-
Coke	-	19.61	-	-	-	-	-	-
Extract	-	-	-	9.81	-	-	-	-
Feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	-

Comparable problems were also encountered in the guardcase operations, requiring two hydrotreating steps to be performed with the concomitant high hydrogen consumption, gas production, and liquid losses. Since this sample was initially targeted for JP-8 production, the entire IPB to 600°F sample was charged to the reforming operation. The product reformate was aromatic saturated in toto.

After examination of the final properties of this material, and in accordance with discussions held with the contract monitor, this sample was scheduled for use as a broad-range, combined fuel fraction. Properties are shown in Table V-20.

Problems were encountered with this material in each of the product quality processing sections. Poor response to guardcase hydrotreating resulted in a rehydrotreatment requirement. Second, even though good (42 volume percent aromatics) reformate was produced, the resulting freeze point of -55°F was disappointing. And finally, the aromatic saturation study produced a relatively high aromatic content fuel. Sample contamination may well have been a problem in this entire sequence.

The overall yield structure is one, however, which more closely approaches the process design capabilities of EXTRACTACRACKING than did sample M-212. As shown in Table V-21, 38 weight percent (43 volume percent) of the crude shale oil was actually produced as final fuel, with an additional fuel potential of 3.7 weight percent light ends loss and 26

TABLE V-20

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No.	M-221
Fuel Type	Broad Range
Shale Source	Above Ground
Gravity, API	43.3
Hydrogen, Wt%	13.6
Saturates, Vol%	66.0
Olefins, Vol%	1.0
Aromatics, Vol%	33.0
Freeze Point, °F	—54
RVP, PSI	
Flash Point, °F	
Heat of Combustion, BTU/#	18,474
Distillation, °F	
IBP	225
10%	299
20%	330
50%	402
90%	496
FBP	536
Residue	1.0
Loss	1.0

TABLE V-21

M-221 ACTUAL YIELDS

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.49	-	0.06	-	0.08	-	-	0.63
NH_3	0.24	-	0.25	-	0.17	-	-	0.66
H_2O	0.79	-	0.04	-	-	-	-	0.83
H_2	-1.52	0.16	-0.31	-	-0.48	0.62	-0.44	-1.97
C_1	-	0.63	0.02	-	-	0.28	0.10	1.03
C_2	0.73	1.40	0.19	-	0.16	0.23	-	2.71
C_3	0.65	0.50	0.18	-	0.32	0.45	0.05	2.15
C_3=	-	1.59	-	-	-	-	-	1.59
C_4	0.50	0.51	0.10	-	0.27	0.27	0.30	1.95
C_4=	-	1.91	-	-	-	-	-	1.91
C_5	0.89	-	0.06	-	0.31	0.14	0.46	1.86
C_5+ Losses	-	1.88	-	-	1.84	-	-	3.72
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	25.61	22.23	-	43.15	40.48	38.49	38.02	38.02
Separated Diesel	-	-	-	-	-	-	-	-
600+	71.62	26.77	26.18	-	-	-	-	26.18
Coke	-	14.04	-	-	-	-	-	14.04
Extract	-	-	-	4.69	-	-	-	4.69
Feed	100.00	71.62	26.77	47.84	43.15	40.48	38.49	100.00

weight percent residuum. Hydrogen consumption was only 1200 SCFB, compared to the high value obtained for sample M-212. If proper operation of the aromatic saturation module had been obtained, a broad-range fuel of 14.0 weight percent hydrogen would have accrued at a total process hydrogen consumption of 1300 SCFB. Overall results for this sample were disappointing though in the high (14 weight percent of shale) coke yield. This failure to provide good coke control is primarily attributable to mechanical limitations, although several obvious processing condition modifications could also improve this value.

Table V-22 and Figure V-5 demonstrate the potential yield structure based on these data on a no-loss basis when practicing recycle. A total of 51.7 weight (59.4 volume) percent of crude shale feed would be obtained as broad-range turbine fuel. Hydrogen cost would again be about 1200 SCFB without modification to the high aromatic content observed.

SAMPLE GC-2

Sample GC-2 was provided as the best simulation possible of expected actual plant practice. The production method was by concurrent preparation of all pertinent military fuel samples, plus the use of aging test products to simulate true steady-state and/or average catalyst age products. Further, this sample was also designed to test feeding full range hydrotreater products to the FCC unit.

TABLE V-22

M-221 NO-LOSS YIELDS WITH RECYCLE

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.49	-	0.07	-	0.11	-	-	0.67
NH_3	0.24	-	0.31	-	0.22	-	-	0.77
H_2O	0.79	-	0.05	-	-	-	-	0.84
H_2	-1.52	0.32	-0.38	-	-0.63	0.85	-0.60	-1.96
C_1	-	1.36	0.03	-	-	0.39	0.13	1.91
C_2	0.73	2.32	0.23	-	0.20	0.32	-	3.80
C_3	0.65	1.00	0.22	-	0.42	0.61	0.06	2.96
C_3=	-	2.41	-	-	-	-	-	2.41
C_4	0.50	1.22	0.12	-	0.35	0.36	0.41	2.96
C_4=	-	2.61	-	-	-	-	-	2.61
C_5	0.89	0.54	0.07	-	0.40	0.19	0.62	2.71
C_5+ Losses	-	-	-	-	-	-	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	25.61	36.59	-	56.10	55.03	52.31	51.69	51.69
Separated Diesel	-	-	-	-	-	-	-	-
600+	71.62	6.20	6.07	-	-	-	-	6.07
Coke	-	16.46	-	-	-	-	-	16.46
Extract	-	-	-	6.10	-	-	-	6.10
Feed	100.00	97.80	32.97	62.20	56.10	55.03	52.31	100.00

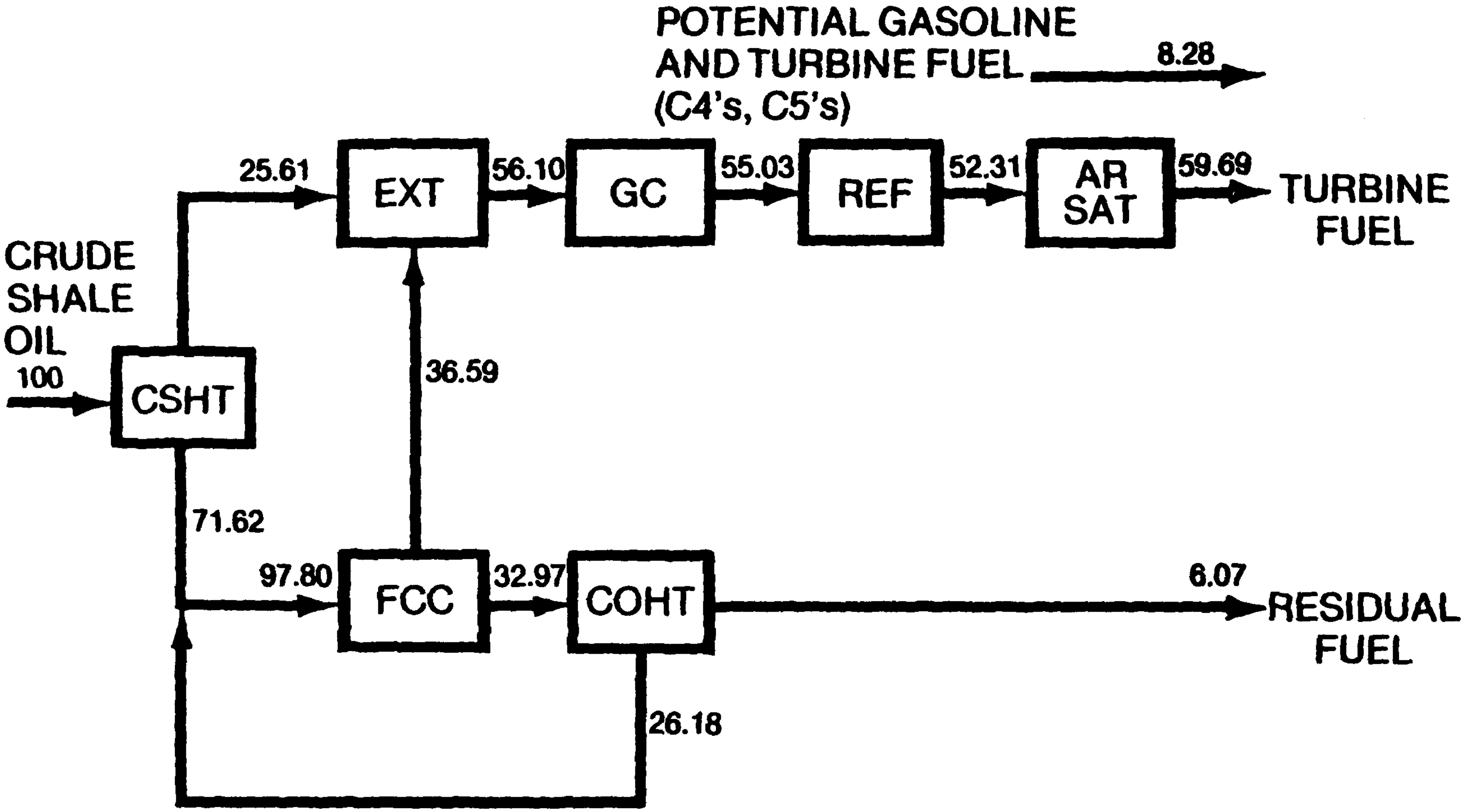

Figure V-5. Sample M-221 – Target: Broad-range Turbine Fuel

The crude shale oil was hydrotreated over cobalt molybdate catalyst at estimated optimum conditions for a nominal period of 30 days. Product composites covering the entire run were stabilized and fed to the FCC unit without fractionation.

The FCC distillate was extracted as before and the extraction raffinate provided to the guardcase. During this sequence, however, a new, specially designed raffinate cleanup system was used to provide a non-contaminated feed to the guardcase.

The guardcase operation was performed by incrementally increasing severity to define actual minimum severity necessary to produce 1 ppm sulfur and nitrogen product. Due to the slow analytical turnaround, however, and expectations based on previous (contaminated) sample requirements, required conditions were attained very early and overshot by a significant margin. When this fact was discovered, conditions were frozen and the run continued to the end of feed (~4 days). No aging was noted, as might be expected due to the higher than required conditions used. At this point, the best estimate available for removal of diesel fractions was used. Two and one-half weight percent of the guardcase product was removed as 580°F+ nominal bottoms.

This -580°F distillate was processed through the reformer under accelerated aging conditions approximating two months of commercial operation. The entire product was composited, stabilized and aromatic saturated to a very low level of total aromatics.

This composite sample was then fractionated into pseudocomponents and pertinent fuel samples prepared by blending.

Table V-23 shows yield structures encountered during these studies, and Table V-24 actual overall process yields. While the overall process yield structure is biased negatively by the excessive severity in the guard-case and reformer (due to other objectives) the conversion module is appropriate for comparison to M-212 and M-221. For this sample, distillate (I to 600°F) and, in particular, light distillate (I to 400°F) yields from the FCC were suppressed at 10 to 12 weight percent of crude shale oil by inclusion of distillate material in the feed. Extract and total nitrogen content of the extraction module feed were, however, reduced. There may be further advantages of processing the above-ground material in this manner which will be explored elsewhere.

Hydrogen consumption for this process was roughly 1600 SCFB of crude shale oil feed. Of particular interest, however, was the very low aromatics content of the C_6 to 600°F heartcut. Other than the previously postulated potential contamination of earlier samples, no explanation is readily available for the better saturation response of this material.

TABLE V-23

GC-2 YIELD STRUCTURE

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO-TAL
H_2S	0.42	-	-	-	0.24	-	-	-
NH_3	0.22	-	-	-	0.32	-	-	-
H_2O	0.74	-	-	-	-	-	-	-
H_2	-1.74	0.22	-	-	-1.75	0.75	-2.27	-
C_1	0.08	0.53	-	-	0.04	0.88	-	-
C_2	0.22	1.05	-	-	0.43	1.62	-	-
C_3	0.17	0.51	-	-	0.62	2.20	0.14	-
C_3=	-	1.25	-	-	-	-	-	-
C_4	0.14	0.47	-	-	0.59	1.23	0.49	-
C_4=	-	1.52	-	-	-	-	-	-
C_5	0.03	-	-	-	1.31	0.40	0.47	-
C_5+ Losses	-	1.10	-	-	0.49	-	-	-
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	99.72	37.23	-	90.65	95.25	92.92	101.17	-
Separated Diesel	-	-	-	-	2.46	-	-	-
600+	-	40.39	-	-	-	-	-	-
Coke	-	15.73	-	-	-	-	-	-
Extract	-	-	-	9.35	-	-	-	-
Feed	100.00	-	-	-	-	-	-	-

TABLE V-24

GC-2 ACTUAL YIELDS

	CSHT	FCC	COHT	EXT	GC	REF	AR SAT	TO- TAL
H_2S	0.42	-	-	-	0.08	-	-	0.50
NH_3	0.22	-	-	-	0.11	-	-	0.33
H_2O	0.74	-	-	-	-	-	-	0.74
H_2	-1.74	0.22	-	-	-0.59	0.24	-0.68	-2.55
C_1	0.08	0.53	-	-	0.01	0.28	-	0.90
C_2	0.22	1.05	-	-	0.14	0.52	-	1.93
C_3	0.17	0.51	-	-	0.21	0.71	0.04	1.64
$C_3=$	-	1.25	-	-	-	-	-	1.25
C_4	0.14	0.47	-	-	0.20	0.39	0.15	1.35
$C_4=$	-	1.52	-	-	-	-	-	1.52
C_5	0.03	-	-	-	0.44	0.13	0.14	0.74
C_5+ Losses	-	1.10	-	-	0.16	-	-	1.26
Separated Gasoline	-	-	-	-	-	-	-	-
C_6-600 or Heartcut	99.72	37.12	-	37.65	32.06	29.79	30.14	30.14
Separated Diesel	-	-	-	-	0.83	-	-	0.83
600+	-	40.26	-	-	-	-	-	40.26
Coke	-	15.69	-	-	-	-	-	15.69
Extract	-	-	-	3.47	-	-	-	3.47
Feed	100.00	99.72	-	37.12	33.65	32.06	29.79	100.00

Better gas production control was obvious during this run. However, aforementioned coke management problems yet again resulted in an unacceptably high overall coke rate.

As was practical for the earlier GC-1 sample, component streams were again produced and finished fuels blended. In this case, JP-4, JP-5 and JP-8 specification fuels were prepared in addition to the diesel stream. Tables V-25 through V-27 present the properties for each product sample. Relatively equal yields of each turbine fuel were encountered. With recycle provisions, the relative and total yield of JP-4, in particular, would be increased. Figure V-6 presents a calculated recycle case.

CONCLUSIONS

Based on these data only, the following conclusions can be drawn:

- Front end hydrotreating over cobalt molybdate catalyst again appears to be favored over nickel molybdate catalyst, but by a much smaller margin. There are indications, to be developed further in the experimental section of this report, that the nickel molybdate may, in fact, be favored for the optimum case.
- Feeding a full range feedstock to the FCC unit again appears to be less favorable than the fractionation case. Quality of the product, however, was improved.

TABLE V-25

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No.	GC 2-4	
Fuel Type	JP-4	
Shale Source	Above-Ground	
		Specifications
Gravity, API	54.3	45-57
Hydrogen, Wt%	14.9	13.6 min
Saturates, Vol%	97.9	
Olefins, Vol%	0.4	
Aromatics, Vol%	1.7	25.0 max
Freeze Point, °F	—90	—72 max
RVP, PSI	2.1	2-3
Flash Point, °F		
Heat of Combustion, BTU/#	18,820	18,400 min
Distillation, °F		
IBP	152	
10%	228	
20%	247	
50%	285	
90%	359	
FBP	412	
Residue	1.0	
Loss	1.0	

TABLE V-26

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No.	GC2-5	
Fuel Type	JP-5	
Shale Source	Above-Ground	
		Specifications
Gravity, API	43.3	36-48
Hydrogen, WT%	14.2	13.5 min
Saturates, Vol%	92.4	
Olefins, Vol%	0.7	
Aromatics, Vol%	6.9	25.0 max
Freeze Point, °F	—68	—51 max
RVP, PSI		
Flash Point, °F	146	140 min
Heat of Combustion, BTU/#	18,648	18,300 min
Distillation, °F		
IBP	356	
10%	380	
20%	388	
50%	405	
90%	439	
FBP	452	
Residue	1.0	
Loss	0.5	

TABLE V–27

AVIATION TURBINE FUEL FROM CRUDE SHALE OIL PHASE II

Sample No.	GC2-8	
Fuel Type	JP-8	
Shale Source	Above-Ground	
		Specifications
Gravity, API	43.6	37-51
Hydrogen, Wt%	14.2	13.6 min
Saturates, Vol%	92.1	
Olefins, Vol%	0.8	
Aromatics, Vol%	7.1	25.0 max
Freeze Point, °F	—60	—58 max
RVP, PSI		
Flash Point, °F	130	100 min
Heat of Combustion, BTU/#	18,659	18,400 min
Distillation, °F		
IBP	338	
10%	367	
20%	377	
50%	407	
90%	466	
FBP	502	
Residue	1.0	
Loss	0.5	

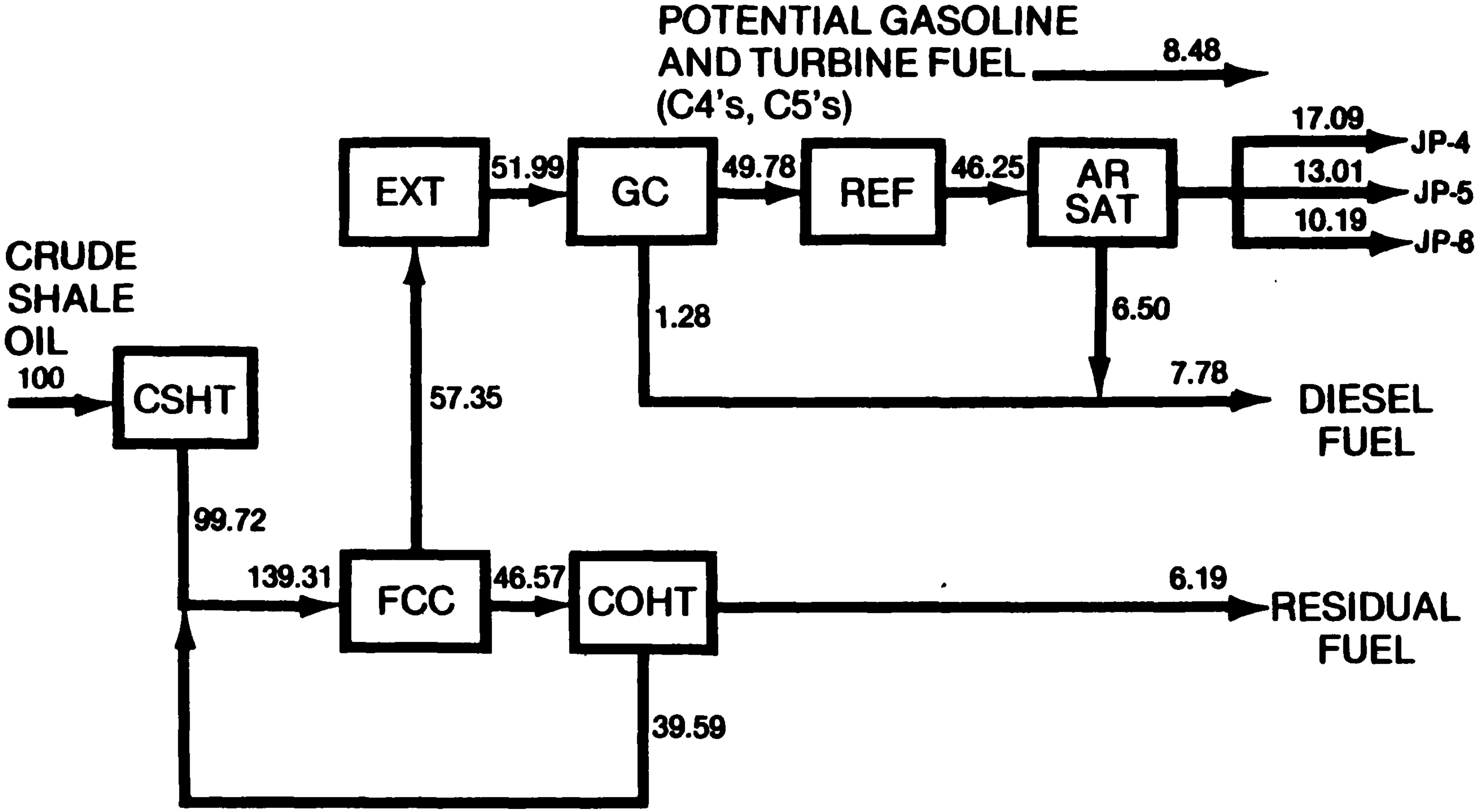

Figure V-6. Sample GC-2 – Concurrent Fuel Production

- Optimum operating conditions for processing this above-ground material are probably at higher severity than utilized for production of these samples.

3. Comparison of In Situ and Above-Ground Samples. As a result of the required program design and limited time availability for this program, three samples each of in situ and above-ground oils were processed at comparable conditions. The products and processing responses can, therefore, be directly compared at comparable operating conditions. The reader should note, however, that this methodology may bias the evaluation against the above-ground oil, since conditions, in most cases, were selected based on experience with the in situ type material. Selection of conditions more suited for the above-ground oil could be expected to improve the yield results significantly. This comparison, however, does allow a good relative response evaluation of each oil to analogous conditions.

The in situ oil produces higher distillate yields, at lower gas production, hydrogen consumption, coke make, and extract yield than the above-ground oil at equivalent operating conditions. Feeding full-range hydrotreated stocks to the FCC, however, produces equivalent total liquid yields. This option, with better definition of preferred conditions, could, in fact, be a selected processing method for the above-ground material.

Product quality considerations show little or no basis for selection of one oil over the other. Subjectively, however, the above-ground oil blended to specification with fewer problems than the in situ material. This observation is tempered by the slightly higher severities required for specification processing of the above-ground oil.

Overall, the in situ oil appears to be the preferred feedstock due to the relative ease with which higher distillate yields are obtained. Better selection of conditions, however, and in particular, better coke management practices, would be expected to improve the performance of the above-ground material. Both oils are acceptable feedstocks to the EXTRACTACRACKING process.

SECTION VI

OVERVIEW AND CONCLUSIONS

The original task definitions for Phase II were shown in Figure III-1. These tasks have been completed successfully, with all requirements met or exceeded.

The Phase II work reported herein is particularly significant in that no major changes or negative results resulted when compared with our original expectations. In fact, Phase II has demonstrated, as shown in Figure VI-1, that there is a distinct possibility of actually improving over the yields estimated during Phase I. Phase II data shown are somewhat optimistic, in that minimum gas and coke production data are used for the FCC estimate, and minimized hydrocarbon loss at maximum nitrogen removal provided in the extraction calculations. Further, nitrogen extract is assumed to be used in that calculation for a portion of the plant hydrogen requirements. For those reasons, the estimate is probably an upper limit on potential plant yields. However, it does graphically demonstrate that the Phase I yield estimates should be attainable, and, in fact, may well be exceeded by proper plant configuration and operation.

Major highlights of the Phase II work include:

TABLE VI-1

COMPARISON OF POTENTIAL YIELDS FROM PHASES I AND II

BASIS: 100,000 BPD IN SITU SHALE OIL

Net Products	Yield Estimate, Volume Percent	
	Phase I	Phase II
Propane	0.6	2.8
Propylene	7.0	5.6
i Butane	2.1	4.2
n Butane	1.0	2.5
Butylenes	4.9	2.9
Gasoline	20.1	24.4
Turbine Fuel	54.4	51.8
Diesel Fuel	0.0	7.1
Residual Fuel	5.0	2.6
Total	95.1	103.9

Crude Shale Hydrotreater:

1. A slight hydrotreater severity increase over that estimated for Phase I is probably optimum for the in situ material.
2. The above-ground material will require higher pressure operation than the in situ stock to maintain catalyst activity.
3. Limitation of hydrogen consumption, control of sulfur content, and basic nitrogen control in desired directions were demonstrated.

Fluid Catalytic Cracker:

1. Reasonable, stable operation on very high nitrogen feedstocks was successfully demonstrated.
2. Denitrogenation and hydrogen redistribution factors were demonstrated.
3. If recycle hydrotreating is practiced, fresh feed and recycle streams will probably be processed separately. Further, the fresh feed cracker would be operated at low (40 to 60 percent) conversion, and the recycle cracker at high (70 to 90 percent) conversion.
4. An exciting potential for use of nitrogen extract in the FCC unit has been indicated, which requires further examination during Phase III.

5. At equal conversion and production hydrotreating conditions, the in situ and above-ground oils appear to be very similar in overall crackability. Yield distributions do, however, differ.

Nitrogen Extraction:

1. Operating conditions have been defined for maximizing nitrogen removal while minimizing hydrocarbon loss.
2. Not only has the process proven applicable to catalytically cracked stocks, but the catalytically cracked material has been shown to be a superior extraction charge when compared to the hydrotreated straight run material.
3. In terms of extraction response, the two crude shale oils are comparable when produced at comparable conditions. The in situ raffinate is superior in quality (primarily due to lower nitrogen content) to the above-ground.

Recycle Hydrotreating:

1. Hydrotreated recycle material has been demonstrated to be a superior cracker chargestock.
2. Sulfur content of FCC bottoms has proven to be more refractory towards hydrotreating than in the original crude shale oil, but the nitrogen is equivalent.

3. Final definition of actual recycle hydrotreater configuration and use will be determined by Phase III results and Phase IV costs.

Guardcase Hydrotreating:

1. Successful operation on properly prepared materials was demonstrated at conditions analogous to those estimated during Phase I.
2. The above-ground material requires slightly higher severity than the in situ feedstock.
3. Freeze points of the guardcase products are very similar to those estimated during Phase I.

Freeze Point Modification:

1. Freeze point modifications ranging from 10 to 20°F were obtained.
2. Product aromatics contents were remarkably similar, irrespective of feed source.
3. Aging character of the in situ feedstock was acceptable, but the above-ground aging was not.

Aromatic Saturation:

1. Product aromatic levels as low as 6 percent were attained (85 percent saturation).
2. Results were somewhat erratic between samples.

Sample Quality:

1. Excellent sample quality was attained.
2. Quality of the samples was, in fact, excessive; higher yields and lower costs can readily be provided.
3. There is no significant product quality difference between oils.

Overall, these results confirm both the original process design and the Phase II work.

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